



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
 15.07.1998 Bulletin 1998/29

(51) Int. Cl.<sup>6</sup>: **H01M 4/62, H01M 4/48,  
 H01M 4/58**

(21) Application number: **97122297.1**

(22) Date of filing: **17.12.1997**

(84) Designated Contracting States:  
**AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC  
 NL PT SE**  
 Designated Extension States:  
**AL LT LV MK RO SI**

(30) Priority: **20.12.1996 JP 341012/96  
 10.03.1997 JP 54947/97  
 04.06.1997 JP 163285/97**

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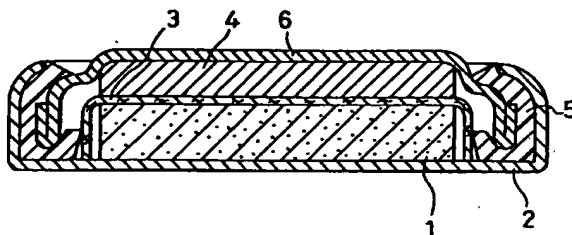
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(54) **Non-aqueous electrolyte secondary battery**

(57) The present invention provides a non-aqueous electrolyte secondary battery having an anode active material with a high capacity and excellent cycle characteristics. The active material comprises a salt generated reacting a metal or a semi-metal and a compound selected from the group consisting of oxo-acids, thiocyanic acid, cyanogen, and cyanic acid, wherein each

said oxo-acid comprises an element selected from the group consisting of nitrogen, sulfur, carbon, boron, phosphorus, selenium, tellurium, tungsten, molybdenum, titanium, chromium, zirconium, niobium, tantalum, manganese, and vanadium, salts of said oxo-acids of phosphorus and boron being restricted to hydrogen-phosphates and hydrogenborates.

**FIG. 1**



## Description

## BACKGROUND OF THE INVENTION

5 The present invention relates to an improvement in anodes of non-aqueous electrolyte secondary batteries.

Non-aqueous electrolyte secondary batteries including lithium or a lithium compound for the anode are expected to have a high voltage and high energy density, and therefore, they are extensively studied.

Known cathode active materials for the non-aqueous electrolyte secondary batteries are oxides and chalcogens of transition metals, such as  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Cr}_2\text{O}_5$ ,  $\text{MnO}_2$ ,  $\text{TiS}_2$ ,  $\text{MoS}_2$  and the like. These compounds  
10 have a layered or tunneled crystal structure to allow lithium ions to freely intercalate and deintercalate. The use of metallic lithium for the anode active material has intensively been examined. Such use, however, has a drawback; lithium dendrite occurring on the surface of metallic lithium in the course of charging results in lowering the charge-discharge efficiency and may come into contact with the cathode to cause an inner short circuit.

In order to solve this problem, the potentials for application of lithium alloys, such as lithium-aluminum, which can  
15 depress the growth of lithium dendrite and absorb and desorb lithium, for the anode have been studied. However, when lithium alloys are used for the anode, repeated charge and discharge causes pulverization of the alloys, posing a problem of poor cycle life characteristics.

There are proposals for solving this problem by inhibiting pulverization of the alloys by including additional elements in the lithium-aluminum alloy (for example, Japanese Laid-Open Patent Publication Sho 62-119856 and Hei 4-109562),  
20 although the improvement is not sufficient. Lithium ion batteries recently developed have anodes composed of carbon material that reversibly intercalates and deintercalates lithium and has excellent cycle characteristics and safety though having a smaller capacity than those of the anode active materials mentioned above.

With a view to enhancing the capacity, a number of studies have proposed application of oxides for the anode; for example, crystalline oxides, such as  $\text{SnO}$  and  $\text{SnO}_2$  (Japanese Laid-Open Patent Publication Hei 7-122274 and Hei 7-235293) and amorphous oxides, such as  $\text{SnSiO}_3$ ,  $\text{SnSi}_{1-x}\text{P}_x\text{O}_3$  (Japanese Laid-Open Patent Publication Hei 7-288123). These oxides, however, do not sufficiently improve the characteristics.

## SUMMARY OF THE INVENTION

30 The object of the present invention is thus to provide an anode for non-aqueous electrolyte secondary batteries having excellent charge-discharge cycle characteristics.

The present invention provides an anode that absorbs lithium in the course of charging not to cause dendrite and has a large electric capacity and an excellent cycle life.

The present invention is directed to a non-aqueous electrolyte secondary battery comprising a cathode capable of  
35 being charged and discharged, a non-aqueous electrolyte, and an anode capable of being charged and discharged, the anode having an active material that comprises a salt of a metal or a semi-metal and a compound selected from the group consisting of an oxo-acid, thiocyanic acid, cyanogen, and cyanic acid, wherein the oxo-acid is one of an element selected from the group consisting of nitrogen, sulfur, carbon, boron, phosphorus, selenium, tellurium, tungsten, molybdenum, titanium, chromium, zirconium, niobium, tantalum, manganese, and vanadium.

40 It is preferable that the metal or the semi-metal constituting the metal salt or the semi-metal salt is at least one selected from the group consisting of Al, Sn, Si, Pb, Cd, Bi, In, Zn, Mg, Ge, Ga, Ca, Ba, Ir, Sb, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Mo, W, and Nb. Especially preferable are Sn, Pb, In, and Bi.

The present invention gives a non-aqueous electrolyte secondary battery that is free from a short circuit due to dendrite and has a high energy density, an excellent cycle life, and a high reliability.

45 While the novel features of the invention are set forth particularly in the appended claims, the invention, both as to organization and content, will be better understood and appreciated, along with other objects and features thereof, from the following detailed description taken in conjunction with the drawings.

## BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

50 Fig. 1 is a vertical sectional view schematically illustrating a test cell used for evaluating the electrode characteristics of active materials in accordance with the present invention.

Fig. 2 is a vertical sectional view schematically illustrating a cylindrical battery including an anode in accordance with the present invention.

## DETAILED DESCRIPTION OF THE INVENTION

As discussed above, the anode of the present invention comprises a metal salt or a semi-metal salt of a specific

acid or cyanogen.

In the following description, salts of a divalent metal  $M^{II}$  are given as examples. Salts of nitrogen oxo-acids include nitrates  $M^{II}(NO_3)_2$  and nitrites  $M^{II}(NO_2)_2$ .

Salts of sulfur oxo-acids include sulfates  $M^{II}SO_4$ , sulfites  $M^{II}SO_3$ , disulfates  $M^{II}S_2O_7$ , peroxomonosulfates  $M^{II}SO_5$ , peroxodisulfates  $M^{II}S_2O_8$ , thiosulfates  $M^{II}S_2O_3$ , disulfites  $M^{II}S_2O_5$ , thiosulfites  $M^{II}S_2O_2$ , hydrogensulfates such as  $M^{II}(HSO_4)_2$ , thionates such as dithionates  $M^{II}S_2O_6$  and dithionites  $M^{II}S_2O_4$ , sulfoxylates such as  $M^{II}SO_2$ , and hydrogen-containing acid salts.

Preferable salts of phosphorus oxo-acids include hydrogenphosphates such as  $M^{II}HPO_4$  and  $M^{II}(H_2PO_4)_2$ , phosphinates  $M^{II}(PH_2O_2)_2$ , and phosphonates  $M^{II}PHO_3$ .

Salts of carbon oxo-acids include carbonates  $M^{II}CO_3$  and hydrogencarbonates  $M^{II}(HCO_3)_2$ .

Preferable salts of boron oxo-acids include hydrogenborates such as  $M^{II}(H_2BO_3)_2$  and  $M^{II}HBO_3$ .

Salts of selenium oxo-acids include selenates  $M^{II}SeO_4$ , selenites  $M^{II}SeO_3$ ,  $M^{II}SeO_5$ , hydrogenselenates  $M^{II}(HSeO_4)_2$ , and hydrogenselenites  $M^{II}(HSeO_3)_2$ .

Salts of tellurium oxo-acids include tellurates such as  $M^{II}_3TeO_6$  and  $M^{II}TeO_4$ , and hydrogentellurates such as  $M^{II}_5(H_5TeO_6)_2$ ,  $M^{II}_2H_2TeO_6$ ,  $M^{II}_3(H_3TeO_6)_2$ , and  $M^{II}H_4TeO_6$ .

Available thiocyanates include  $M^{II}(SCN)_2$ , while available cyanides and cyanates include  $M^{II}(CN)_2$  and  $M^{II}(ONC)_2$ .

The metal salt and the semi-metal salt of the present invention are, however, not restricted to the above chemical compositions.

Among the above salts, sulfates, hydrogensulfates, carbonates, hydrogenborates, and hydrogenphosphates are preferable for the improvement in cycle characteristics.

The following gives salts of oxo-acids of transition elements W, Mo, Ti, Zr, Nb, Ta, Mn, and V as examples. In the following formulae,  $M^{III}$  represents a trivalent metal or semi-metal.

Available tungstates include  $M^{III}WO_4$ ,  $M^{III}WO_3$ ,  $M^{III}WO_6$ . Available molybdates include  $M^{III}MoO_4$  and  $M^{III}Mo_4O_6$ . Available titanates include  $M^{III}TiO_3$ ,  $M^{III}TiO_4$ ,  $(M^{III})_2TiO_5$ , and  $M^{III}Ti_3O_7$ .

Available zirconates include  $M^{III}ZrO_3$  and  $M^{III}ZrO_4$ . Available chromates include  $M^{III}CrO_3$ ,  $M^{III}CrO_4$ ,  $M^{III}Cr_2O_4$ , and  $(M^{III})_2CrO_6$ . Available niobates include  $M^{III}NbO_4$ ,  $M^{III}Nb_2O_6$ , and  $(M^{III})_2Nb_2O_7$ .

Available tantalates include  $M^{III}TaO_4$  and  $(M^{III})_2Ta_2O_7$ . Available manganates include  $M^{III}MnO_3$ ,  $(M^{III})_2MnO_4$ , and  $(M^{III})_2MnO_6$ . Available vanadates include  $M^{III}VO_4$ ,  $(M^{III})_2VO_5$ , and  $M^{III}V_2O_6$ .

Preferable are chromates, tungstates, molybdates, vanadates, manganates, and tantalates, and especially preferable are chromates, tungstates, and molybdates for the improvement in cycle characteristics.

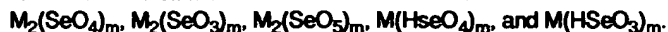
The metal salt and the semi-metal salt of the present invention are, however, not restricted to the above chemical compositions.

The present inventors have made an intensive study on the availability of various metal salts and semi-metal salts as the negative electrode material. It was found that such compounds can serve as the negative electrode materials with a high capacity and exceptional cycle life characteristics that have a crystal structure in which the metal or semi-metal is surrounded by a) the salts including oxygen and any one of nitrogen, sulfur, phosphorus, carbon, boron, selenium, and tellurium, such as salts of oxo-acids of nitrogen, sulfur, phosphorus, carbon, boron, selenium and tellurium or by the salts further including hydrogen such as hydrogen-containing oxo-acids; b) cyanides containing nitrogen and carbon; c) cyanates containing nitrogen, carbon and oxygen; or d) thiocyanates containing nitrogen, carbon and sulfur and in which those salts are bonded to the metal or semi-metal by ionic force.

The present inventors also discovered that such compounds can also serve as the negative electrode materials with a high capacity and superb cycle life characteristics that have a crystal structure in which the metal or semi-metal is surrounded by the salts of oxo-acid of a transition element including oxygen and any one of tungsten, molybdenum, titanium, chromium, zirconium, niobium, tantalum, manganese and vanadium, that is, tungstates, molybdates, titanates, zirconates, chromates, niobates, tantalates, manganates and vanadates.

The prior art metal oxides have the greater tendency of covalent bonding and tougher skeletons than those of the metal salts and semi-metal salts in accordance with the present invention. While the prior art metal oxides are presumed to be relatively brittle under the conditions of expansion and contraction accompanied by intercalation and deintercalation of a large amount of lithium, however, the metal salts and semi-metal salts of the present invention are expected to be relatively tough under the conditions of expansion and contraction accompanied by intercalation and deintercalation of a large amount of lithium. It is also found that the existence of hydrogen in the salts of oxo-acids further improves the cycle characteristics, although the details have not yet been elucidated.

The chemical compositions of the metal salts and the semi-metal salts discussed above represent only examples of divalent or trivalent metals and semi-metals. Chemical compositions of metal salts and semi-metal salts of different valences should be apparent to the skilled in the art. For example, selenates can be expressed by the following general formulae as the metal salts and semi-metal salts of the valence m:



Some examples in accordance with the present invention are given below, although the anode material of the

present invention is not restricted to the chemical compositions discussed in these examples.

#### Example 1

Test cells shown in Fig. 1 were manufactured and tested for evaluation of the electrode characteristics of various metal and semi-metal nitrates and nitrites specified in Tables 1 and 2 and used as the anode active material.

Referring to Fig. 1, numeral 1 designates a test electrode composed of a molded mixture containing an active material. The test electrode 1 is arranged on the substantial center of a battery casing 2. A separator 3 of a micro-porous polypropylene film was placed on the test electrode 1. After injection of an electrolyte solution, the opening of the battery casing 2 is sealed with a sealing plate 6 having a counter electrode 4 composed of a metallic lithium disc of 17.5 mm in diameter on the inner surface thereof and a polypropylene gasket 5 on the circumference thereof. This completes a test cell.

The mixture included 6 g of an active material powder, 3g of graphite powder as a conductive agent, and 1 g of polyethylene powder as a binding agent. The test electrode 1 was obtained by press molding 0.1 g of the mixture to a disc of 17.5 mm in diameter. The electrolyte used was prepared by dissolving lithium perchlorate ( $\text{LiClO}_4$ ) at a concentration of 1 mol/l in a 1:1 mixed solution (volume ratio) of ethylene carbonate and dimethoxyethane.

At a constant electric current of 2 mA, the test cell was subjected to cathode polarization (which corresponds to charging in case that the active material-containing electrode is considered as the anode) until the electrode potential became 0 V with respect to the lithium counter electrode. The test cell was then subjected to anode polarization (which corresponds to discharging) until the electrode potential became 1.5 V with respect to the counter electrode. After the repeated cathode polarization and anode polarization, and the electrode characteristics were evaluated.

For the purpose of comparison, electrodes were manufactured in the above manner using the known compounds shown in Table 3, that is, crystalline oxides  $\text{WO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{SnO}$ , and  $\text{PbO}$ , sulfides  $\text{SnS}$  and  $\text{PbS}$ , and amorphous metal oxides  $\text{SnSiO}_3$  and  $\text{SnSi}_{0.8}\text{P}_{0.2}\text{O}_{3.1}$ , and test cells were assembled and tested under the same conditions for evaluation of the electrode characteristics.

Tables 1 through 3 show the discharge capacities per one gram of the active material in the first cycle.

The measurement proved that all the test cells of Example 1 were capable of being charged and discharged. After the conclusion of cathode polarization of these test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 1.

The above experiments show that cathode polarization makes lithium absorbed in the electrodes including the active materials of Example 1 and anode polarization makes the absorbed lithium released from the electrodes, thereby causing no deposit of metallic lithium. The electrodes of Example 1 have higher capacities than those of the comparative examples.

Cylindrical batteries shown in Fig. 2 were manufactured and tested for evaluation of the cycle characteristics of the batteries using various metal and semi-metal nitrates and nitrites of Example 1.

Each battery was manufactured in the following manner.

A cathode active material  $\text{LiMn}_{1.8}\text{Co}_0.2\text{O}_4$  was prepared by mixing  $\text{Li}_2\text{CO}_3$ ,  $\text{Mn}_2\text{O}_4$ , and  $\text{CoCO}_3$  at a predetermined molar ratio, heating the mixture at 900 °C, and classifying the mixture to or below 100 meshes.

A paste was prepared by mixing 100 g of the cathode active material, 10 g of carbon powder as a conductive agent, and 8 g (as the resin) of aqueous dispersion of polyethylene tetrafluoride as a binding agent, and pure water. The paste was applied onto a titanium core member, dried, and rolled out to a cathode plate.

An anode plate was manufactured by mixing a metal or semi-metal nitrate or nitrite as an active material, graphite powder as a conductive agent, and Teflon powder as a binding agent at the weight ratio of 60 : 30 : 10, adding a petroleum solvent to the mixture to yield a paste, applying the paste onto a copper core member, and drying it at 100 °C. A micro-porous polypropylene film was used as a separator.

A cathode plate 11 with a cathode lead 14 which is composed of the same material as that of the core member and attached to the cathode plate 11 by spot welding, an anode plate 12 with an anode lead 15 welded thereto, and a separator 13 having a greater width than those of these electrode plates 11 and 12 were wound in spirals to constitute an electrode group. Polypropylene insulating plates 16 and 17 were placed on the top and bottom of the electrode group, and the assembly was inserted into a battery casing 18. After formation of a step on the upper portion of the battery casing 18 and injection of the same non-aqueous electrolyte as that of the above-mentioned test cell, the battery casing 18 was sealed with a sealing plate 19 having an anode terminal 20. This completes a battery.

The batteries constructed as above were subjected to a charge-discharge cycle test at a temperature of 30 °C and a charge-discharge current of 1 mA/cm<sup>2</sup> in a charge-discharge voltage range of 4.3 V to 2.6 V. A rate of the discharge capacity at the 100-th cycle to the discharge capacity at the second cycle (hereinafter referred to as capacity maintenance rate) was measured.

Anode plates were prepared and test batteries were assembled in the above manner for the comparative examples. The cycle characteristics of the comparative examples were also evaluated under the same conditions.

Tables 1 through 3 show the results of evaluation.

Table 1

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
Al(NO <sub>3</sub> ) <sub>3</sub>	284	75
Al(NO <sub>2</sub> ) <sub>3</sub>	326	73
Sn(NO <sub>3</sub> ) <sub>4</sub>	346	86
Sn(NO <sub>2</sub> ) <sub>4</sub>	389	84
Sn(NO <sub>3</sub> ) <sub>2</sub>	485	84
Sn(NO <sub>2</sub> ) <sub>2</sub>	510	82
Si(NO <sub>3</sub> ) <sub>4</sub>	390	83
Si(NO <sub>2</sub> ) <sub>4</sub>	435	84
Pb(NO <sub>3</sub> ) <sub>2</sub>	356	83
Pb(NO <sub>2</sub> ) <sub>2</sub>	394	82
Cd(NO <sub>3</sub> ) <sub>2</sub>	320	78
Cd(NO <sub>2</sub> ) <sub>2</sub>	336	77
Bi(NO <sub>3</sub> ) <sub>3</sub>	298	78
Bi(NO <sub>2</sub> ) <sub>3</sub>	324	75
In(NO <sub>3</sub> ) <sub>3</sub>	346	78
In(NO <sub>2</sub> ) <sub>3</sub>	375	75
Zn(NO <sub>3</sub> ) <sub>2</sub>	289	75
Zn(NO <sub>2</sub> ) <sub>2</sub>	326	79
Ga(NO <sub>3</sub> ) <sub>3</sub>	335	75
Ga(NO <sub>2</sub> ) <sub>3</sub>	362	72
Ge(NO <sub>3</sub> ) <sub>4</sub>	367	74
Ge(NO <sub>2</sub> ) <sub>4</sub>	400	72
Mg(NO <sub>3</sub> ) <sub>2</sub>	296	81
Mg(NO <sub>2</sub> ) <sub>2</sub>	334	79
Sb(NO <sub>3</sub> ) <sub>3</sub>	425	75
Sb(NO <sub>2</sub> ) <sub>3</sub>	433	73
Ti(NO <sub>3</sub> ) <sub>4</sub>	275	80
V(NO <sub>3</sub> ) <sub>2</sub>	255	84
Cr(NO <sub>2</sub> ) <sub>3</sub>	285	82
Mn(NO <sub>3</sub> ) <sub>2</sub>	263	83
Fe(NO <sub>3</sub> ) <sub>2</sub>	274	81
Co(NO <sub>3</sub> ) <sub>2</sub>	269	80
Ni(NO <sub>3</sub> ) <sub>2</sub>	271	80
Cu(NO <sub>3</sub> ) <sub>2</sub>	265	78
Mo(NO <sub>3</sub> ) <sub>2</sub>	222	77
W(NO <sub>3</sub> ) <sub>4</sub>	215	80
Nb(NO <sub>3</sub> ) <sub>3</sub>	220	79
Ca(NO <sub>3</sub> ) <sub>2</sub>	286	79
Ba(NO <sub>3</sub> ) <sub>2</sub>	275	80
Ir(NO <sub>3</sub> ) <sub>3</sub>	266	81
Sr(NO <sub>3</sub> ) <sub>2</sub>	286	79

Table 2

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{Ba}_{0.33}\text{Sn}_{0.67}(\text{NO}_3)_2$	425	86
$\text{Ca}_{0.33}\text{Sn}_{0.67}(\text{NO}_3)_2$	433	85
$\text{Sr}_{0.33}\text{Sn}_{0.67}(\text{NO}_3)_2$	443	85
$\text{Mg}_{0.33}\text{Sn}_{0.67}(\text{NO}_3)_2$	435	85
$\text{Mn}_{0.22}\text{Sn}_{0.78}(\text{NO}_3)_2$	410	86
$\text{Fe}_{0.12}\text{Sn}_{0.88}(\text{NO}_3)_2$	451	85
$\text{Co}_{0.18}\text{Sn}_{0.82}(\text{NO}_3)_2$	444	87
$\text{Cu}_{0.18}\text{Sn}_{0.82}(\text{NO}_3)_2$	435	86
$\text{Ti}_{0.12}\text{Sn}_{0.82}(\text{NO}_3)_2$	436	85
$\text{Zn}_{0.12}\text{Sn}_{0.88}(\text{NO}_3)_2$	442	87
$\text{Cr}_{0.12}\text{Sn}_{0.82}(\text{NO}_3)_2$	440	86
$\text{V}_{0.12}\text{Sn}_{0.82}(\text{NO}_3)_2$	421	87
$\text{Ba}_{0.33}\text{Sn}_{0.67}(\text{NO}_3)_2$	312	85
$\text{Ca}_{0.33}\text{Pb}_{0.67}(\text{NO}_3)_2$	319	87
$\text{Sr}_{0.33}\text{Pb}_{0.67}(\text{NO}_3)_2$	329	87
$\text{Mg}_{0.33}\text{Pb}_{0.67}(\text{NO}_3)_2$	326	85
$\text{Mn}_{0.22}\text{Pb}_{0.78}(\text{NO}_3)_2$	333	84
$\text{Fe}_{0.12}\text{Pb}_{0.88}(\text{NO}_3)_2$	329	86
$\text{Co}_{0.18}\text{Pb}_{0.82}(\text{NO}_3)_2$	326	85
$\text{Cu}_{0.18}\text{Pb}_{0.82}(\text{NO}_3)_2$	319	87
$\text{Ti}_{0.12}\text{Pb}_{0.82}(\text{NO}_3)_2$	314	81
$\text{Zn}_{0.12}\text{Pb}_{0.88}(\text{NO}_3)_2$	329	83
$\text{Cr}_{0.12}\text{Pb}_{0.82}(\text{NO}_3)_2$	320	84
$\text{W}_{0.09}\text{Pb}_{0.82}(\text{NO}_3)_2$	301	87
$\text{Fe}_{0.18}\text{In}_{0.88}(\text{NO}_3)_3$	324	82
$\text{Co}_{0.27}\text{In}_{0.82}(\text{NO}_3)_3$	315	83
$\text{Cu}_{0.27}\text{In}_{0.82}(\text{NO}_3)_3$	310	84
$\text{Ti}_{0.27}\text{Bi}_{0.82}(\text{NO}_3)_3$	275	80
$\text{Zn}_{0.27}\text{Bi}_{0.88}(\text{NO}_3)_3$	284	79

Table 3

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{WO}_2$	190	9

Table 3 (continued)

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{Fe}_2\text{O}_3$	185	10
$\text{SnO}$	522	5
$\text{SnSiO}_3$	453	20
$\text{PbO}$	453	2
$\text{SnS}$	498	6
$\text{PbS}$	436	3
$\text{SnSi}_{0.8}\text{P}_{0.2}\text{O}_{3.1}$	406	25

The batteries using the metal or semi-metal nitrate or nitrite of Example 1 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides.

#### Example 2

Test cells discussed in Example 1 were manufactured and tested under the same conditions as those of Example 1 for evaluation of the electrode characteristics of various metal and semi-metal carbonates and hydrogencarbonates specified in Tables 4 and 5 and used as the anode active material. Tables 4 and 5 show the discharge capacities of the test cells in the first cycle.

The measurement proved that all the test cells of Example 2 were capable of being charged and discharged.

After the conclusion of cathode polarization of these test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 2.

The above experiments show that cathode polarization makes lithium absorbed in the electrodes comprising the active materials of Example 2 and anode polarization makes the absorbed lithium released from the electrodes, thereby causing no deposit of metallic lithium.

Cylindrical batteries discussed in Example 1 were manufactured and tested under the same conditions of those of Example 1 for evaluation of the cycle characteristics of the batteries using various metal and semi-metal carbonates and hydrogencarbonates of Example 2. Tables 4 and 5 show the capacity maintenance rates at the 100-th cycle.

Table 4

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Al_2(CO_3)_3$	342	75
$Al(HCO_3)_3$	306	86
$Sn(CO_3)_2$	493	86
$SnCO_3$	534	82
$Sn(HCO_3)_4$	424	92
$Sn(HCO_3)_2$	490	90
$Si(CO_3)_2$	378	81
$Si(HCO_3)_4$	365	89
$PbCO_3$	441	82
$Pb(HCO_3)_2$	402	84
$CdCO_3$	397	75
$Cd(HCO_3)_2$	365	85
$Bi_2(CO_3)_3$	369	73
$Bi(HCO_3)_3$	305	78
$In_2(CO_3)_3$	461	76
$In(HCO_3)_3$	386	85
$ZnCO_3$	298	72
$Zn(HCO_3)_2$	268	82
$Ga_2(CO_3)_3$	334	73
$Sb(HCO_3)_3$	315	75
$Ga(HCO_3)_3$	312	79
$Ge(CO_3)_2$	365	75
$Ge(HCO_3)_4$	335	83
$MgCO_3$	304	79
$Mg(HCO_3)_2$	292	85
$Ti_2(CO_3)_3$	298	75
$MnCO_3$	263	86



Table 4-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
VCO <sub>3</sub>	198	86
Cr <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	263	82
FeCO <sub>3</sub>	246	84
CoCO <sub>3</sub>	259	83
NiCO <sub>3</sub>	264	81
CuCO <sub>3</sub>	253	82
MoCO <sub>3</sub>	221	82
BaCO <sub>3</sub>	256	80
CaCO <sub>3</sub>	263	75
W(CO <sub>3</sub> ) <sub>2</sub>	215	75
Ir <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	321	73
Sb <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	365	78
Nb(CO <sub>3</sub> ) <sub>5</sub>	187	80
SrCO <sub>3</sub>	273	75

Table 5

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
Ba <sub>0.2</sub> Sn <sub>0.8</sub> CO <sub>3</sub>	498	84
Ca <sub>0.2</sub> Sn <sub>0.8</sub> CO <sub>3</sub>	485	85
Sr <sub>0.2</sub> Sn <sub>0.8</sub> CO <sub>3</sub>	495	85
Mg <sub>0.2</sub> Sn <sub>0.8</sub> CO <sub>3</sub>	500	86
Mn <sub>0.2</sub> Sn <sub>0.8</sub> CO <sub>3</sub>	482	85
Fe <sub>0.2</sub> Sn <sub>0.8</sub> CO <sub>3</sub>	479	87
Co <sub>0.2</sub> Sn <sub>0.8</sub> CO <sub>3</sub>	486	86
Cu <sub>0.2</sub> Sn <sub>0.8</sub> CO <sub>3</sub>	493	85
Ti <sub>0.2</sub> Sn <sub>0.8</sub> CO <sub>3</sub>	475	84
Zn <sub>0.2</sub> Sn <sub>0.8</sub> CO <sub>3</sub>	482	85
Cr <sub>0.2</sub> Sn <sub>0.8</sub> CO <sub>3</sub>	473	85
Mo <sub>0.2</sub> Sn <sub>0.8</sub> CO <sub>3</sub>	459	86
Ba <sub>0.2</sub> Pb <sub>0.8</sub> CO <sub>3</sub>	421	83
Ca <sub>0.2</sub> Pb <sub>0.8</sub> CO <sub>3</sub>	416	85
Sr <sub>0.2</sub> Pb <sub>0.8</sub> CO <sub>3</sub>	416	85
Mg <sub>0.2</sub> Pb <sub>0.8</sub> CO <sub>3</sub>	422	84
Mn <sub>0.2</sub> Pb <sub>0.8</sub> CO <sub>3</sub>	418	87
Fe <sub>0.2</sub> Pb <sub>0.8</sub> CO <sub>3</sub>	409	86
Co <sub>0.2</sub> Pb <sub>0.8</sub> CO <sub>3</sub>	417	85
Cu <sub>0.2</sub> Pb <sub>0.8</sub> CO <sub>3</sub>	415	84
Ti <sub>0.2</sub> Pb <sub>0.8</sub> CO <sub>3</sub>	398	85

Table 5-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
Zn <sub>0.2</sub> Pb <sub>0.8</sub> CO <sub>3</sub>	405	86
Cr <sub>0.2</sub> Pb <sub>0.7</sub> CO <sub>3</sub>	403	85
Mo <sub>0.2</sub> Pb <sub>0.8</sub> CO <sub>3</sub>	398	87
(Fe <sub>0.3</sub> In <sub>0.8</sub> ) <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	415	79
(Co <sub>0.3</sub> In <sub>0.8</sub> ) <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	410	80
(Cu <sub>0.3</sub> In <sub>0.8</sub> ) <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	416	81
(Ti <sub>0.2</sub> Bi <sub>0.8</sub> ) <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	342	78
(Zn <sub>0.3</sub> Bi <sub>0.8</sub> ) <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	331	77
Ba <sub>0.2</sub> Sn <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>2</sub>	452	92
Ca <sub>0.2</sub> Sn <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>2</sub>	441	94
Sr <sub>0.2</sub> Sn <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>2</sub>	443	94
Mg <sub>0.2</sub> Sn <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>2</sub>	451	93
Mn <sub>0.2</sub> Sn <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>2</sub>	443	91
Fe <sub>0.2</sub> Sn <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>2</sub>	439	92
Co <sub>0.2</sub> Sn <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>2</sub>	441	91
Cu <sub>0.2</sub> Sn <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>2</sub>	456	92
Ti <sub>0.2</sub> Sn <sub>0.7</sub> (HCO <sub>3</sub> ) <sub>2</sub>	432	92
Zn <sub>0.2</sub> Sn <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>2</sub>	440	93
Cr <sub>0.2</sub> Sn <sub>0.7</sub> (HCO <sub>3</sub> ) <sub>2</sub>	429	94
Mo <sub>0.2</sub> Sn <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>2</sub>	420	94
Ba <sub>0.2</sub> Pb <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>2</sub>	384	88
Ca <sub>0.2</sub> Pb <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>2</sub>	372	89
Sr <sub>0.2</sub> Pb <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>2</sub>	372	89
Mg <sub>0.2</sub> Pb <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>2</sub>	382	87
Mn <sub>0.2</sub> Pb <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>2</sub>	371	90
Fe <sub>0.2</sub> Pb <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>2</sub>	367	91
Co <sub>0.2</sub> Pb <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>2</sub>	371	90
Cu <sub>0.2</sub> Pb <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>2</sub>	379	89
Ti <sub>0.2</sub> Pb <sub>0.7</sub> (HCO <sub>3</sub> ) <sub>2</sub>	352	89
Zn <sub>0.2</sub> Pb <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>2</sub>	368	90
Cr <sub>0.2</sub> Pb <sub>0.7</sub> (HCO <sub>3</sub> ) <sub>2</sub>	369	90
Mo <sub>0.2</sub> Pb <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>2</sub>	357	91
Fe <sub>0.3</sub> In <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>3</sub>	365	86
Co <sub>0.3</sub> In <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>3</sub>	359	88
Cu <sub>0.3</sub> In <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>3</sub>	358	87
Ti <sub>0.2</sub> Bi <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>3</sub>	301	86
Zn <sub>0.3</sub> Bi <sub>0.8</sub> (HCO <sub>3</sub> ) <sub>3</sub>	286	87

The batteries using the metal or semi-metal carbonate or hydrogencarbonate of Example 2 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides. Especially the use of hydrogencarbonates has remarkably improved the cycle characteristics.

## Example 3

The electrode characteristics of various metal and semi-metal hydrogenborates specified in Tables 6 through 8 and used as the anode active material were evaluated in Example 3.

Test cells discussed in Example 1 were manufactured, and the discharge capacities were measured under the same conditions as those of Example 1. The results of measurement are shown in Tables 6 through 8.

The measurement proved that all the test cells of Example 3 were capable of being charged and discharged.

After the conclusion of cathode polarization of these test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 3.

The above experiments show that cathode polarization makes lithium absorbed in the electrodes comprising the active materials of Example 3 and anode polarization makes the absorbed lithium released from the electrodes, thereby causing no deposit of metallic lithium.

Cylindrical batteries discussed in Example 1 were manufactured, and the capacity maintenance rates at the 100-th cycle were measured under the same conditions as those of Example 1. The results of measurement are shown in Tables 6 through 8.

Table 6

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{Al}_2(\text{HBO}_3)_3$	305	78
$\text{Al}(\text{H}_2\text{BO}_3)_3$	294	80
$\text{SnHBO}_3$	532	83
$\text{Sn}(\text{HBO}_3)_2$	453	85
$\text{Sn}(\text{H}_2\text{BO}_3)_4$	405	86
$\text{Sn}(\text{H}_2\text{BO}_3)_2$	493	85
$\text{Si}(\text{HBO}_3)_2$	326	82
$\text{Si}(\text{H}_2\text{BO}_3)_4$	296	83
$\text{PbHBO}_3$	443	84
$\text{Pb}(\text{H}_2\text{BO}_3)_2$	421	86
$\text{CdHBO}_3$	328	84
$\text{Bi}_2(\text{HBO}_3)_3$	312	79
$\text{Bi}(\text{H}_2\text{BO}_3)_3$	289	81
$\text{In}_2(\text{HBO}_3)_3$	385	84
$\text{In}(\text{H}_2\text{BO}_3)_3$	368	86
$\text{ZnHBO}_3$	268	79
$\text{Zn}(\text{H}_2\text{BO}_3)_2$	268	81
$\text{Ga}_2(\text{HBO}_3)_3$	338	79
$\text{Ga}(\text{H}_2\text{BO}_3)_3$	312	82
$\text{Ge}(\text{HBO}_3)_2$	352	85
$\text{Ge}(\text{H}_2\text{BO}_3)_4$	335	87
$\text{MgHBO}_3$	296	84
$\text{Mg}(\text{H}_2\text{BO}_3)_2$	286	86

Table 7

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Sb_2(HBO_3)_3$	310	80
$Ba_{0.1}Sn_{0.9}HBO_3$	486	84
$Ca_{0.1}Sn_{0.9}HBO_3$	482	85
$Sr_{0.1}Sn_{0.9}HBO_3$	482	85
$Mg_{0.1}Sn_{0.9}HBO_3$	479	84
$Zn_{0.1}Sn_{0.9}HBO_3$	481	86
$Cu_{0.1}Sn_{0.9}HBO_3$	469	87
$Co_{0.1}Sn_{0.9}HBO_3$	467	85
$Fe_{0.1}Sn_{0.9}HBO_3$	461	86
$Ni_{0.1}Sn_{0.9}HBO_3$	449	87
$Ti_{0.2}Sn_{0.7}HBO_3$	459	86
$Cr_{0.1}Sn_{0.7}HBO_3$	449	88
$V_{0.1}Sn_{0.9}HBO_3$	429	87
$Mo_{0.1}Sn_{0.9}HBO_3$	438	87
$W_{0.1}Sn_{0.8}HBO_3$	429	86
$(Mn_{0.3}In_{0.9})_2(HBO_3)_3$	352	82
$(Ni_{0.3}In_{0.8})_2(HBO_3)_3$	357	85
$(Co_{0.3}In_{0.8})_3(HBO_3)_3$	349	85
$(Mn_{0.3}Bi_{0.9})_2(HBO_3)_3$	291	82
$(Ni_{0.3}Bi_{0.8})_2(HBO_3)_3$	281	82
$(Co_{0.3}Bi_{0.8})_3(HBO_3)_3$	279	83

Table 8

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Ba_{0.1}Pb_{0.9}HBO_3$	421	88
$Ca_{0.1}Pb_{0.9}HBO_3$	429	87
$Sr_{0.1}Pb_{0.9}HBO_3$	429	87
$Mg_{0.1}Pb_{0.9}HBO_3$	428	88
$Zn_{0.1}Pb_{0.9}HBO_3$	420	86
$Cu_{0.1}Pb_{0.9}HBO_3$	419	85
$Co_{0.1}Pb_{0.9}HBO_3$	425	84
$Fe_{0.1}Pb_{0.9}HBO_3$	422	85
$Ni_{0.1}Pb_{0.9}HBO_3$	428	86
$Ti_{0.2}Pb_{0.7}HBO_3$	419	89

Table 8 (continued)

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{Cr}_{0.1}\text{Pb}_{0.9}\text{HBO}_3$	401	85
$\text{V}_{0.1}\text{Pb}_{0.9}\text{HBO}_3$	398	87
$\text{Mo}_{0.1}\text{Pb}_{0.9}\text{HBO}_3$	392	86
$\text{W}_{0.1}\text{Pb}_{0.9}\text{HBO}_3$	382	87

The batteries using the metal or semi-metal hydrogenborates of Example 3 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides.

#### Example 4

The electrode characteristics of various salts of oxo-acides of sulfur specified in Tables 9 through 16 and used as the anode active material were evaluated in Example 4.

Tables 9 through 16 show the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 9

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{Al}_2(\text{SO}_4)_3$	389	82
$\text{Al}_2(\text{SO}_3)_3$	405	77
$\text{Al}_2(\text{S}_2\text{O}_7)_3$	342	83
$\text{Al}_2(\text{SO}_5)_3$	370	81
$\text{Al}_2(\text{S}_2\text{O}_8)_3$	338	85
$\text{Al}_2(\text{S}_2\text{O}_3)_3$	375	81
$\text{Al}_2(\text{S}_2\text{O}_6)_3$	364	82
$\text{Al}_2(\text{S}_2\text{O}_5)_3$	372	83
$\text{Al}_2(\text{S}_2\text{O}_2)_3$	378	83
$\text{Al}_2(\text{S}_2\text{O}_4)_3$	364	84
$\text{Al}_2(\text{SO}_2)_3$	415	80
$\text{Sn}(\text{SO}_4)_2$	482	85
$\text{Sn}(\text{SO}_3)_2$	521	80
$\text{Sn}(\text{S}_2\text{O}_7)_2$	416	86

Table 9-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{Sn}(\text{SO}_5)_2$	4 5 6	8 3
$\text{Sn}(\text{S}_2\text{O}_8)_2$	4 0 3	8 4
$\text{Sn}(\text{S}_2\text{O}_3)_2$	4 5 6	8 2
$\text{Sn}(\text{S}_2\text{O}_6)_2$	4 2 3	8 8
$\text{Sn}(\text{S}_2\text{O}_5)_2$	4 3 7	8 7
$\text{Sn}(\text{S}_2\text{O}_2)_2$	4 6 4	8 4
$\text{Sn}(\text{S}_2\text{O}_4)_2$	4 2 4	8 6
$\text{Sn}(\text{SO}_2)_2$	5 1 0	8 2
$\text{SnSO}_4$	5 3 2	8 2
$\text{SnSO}_3$	5 5 6	7 9
$\text{SnS}_2\text{O}_7$	4 8 2	8 5
$\text{SnSO}_5$	5 0 2	8 3
$\text{Al}(\text{HSO}_4)_3$	3 5 6	9 1
$\text{Al}(\text{HSO}_3)_3$	3 7 5	8 7
$\text{Al}(\text{HS}_2\text{O}_7)_3$	3 2 0	9 2
$\text{Al}(\text{HSO}_5)_3$	3 3 5	9 1
$\text{Al}(\text{HS}_2\text{O}_8)_3$	3 1 4	8 9
$\text{Al}(\text{HS}_2\text{O}_3)_3$	3 4 6	8 8
$\text{Al}(\text{HS}_2\text{O}_6)_3$	3 5 2	8 9
$\text{Al}(\text{HS}_2\text{O}_5)_3$	3 4 6	9 0
$\text{Al}(\text{HS}_2\text{O}_2)_3$	3 4 8	9 1
$\text{Al}(\text{HS}_2\text{O}_4)_3$	3 3 4	9 2
$\text{Al}(\text{HSO}_2)_3$	3 5 8	8 9
$\text{Sn}(\text{HSO}_4)_4$	4 4 6	9 5
$\text{Sn}(\text{HSO}_3)_4$	4 5 3	9 2
$\text{Sn}(\text{HS}_2\text{O}_7)_4$	3 8 6	9 4
$\text{Sn}(\text{HSO}_5)_4$	4 2 3	9 3
$\text{Sn}(\text{HS}_2\text{O}_8)_4$	3 7 9	9 4
$\text{Sn}(\text{HS}_2\text{O}_3)_4$	4 3 3	9 3
$\text{Sn}(\text{HS}_2\text{O}_6)_4$	4 0 2	9 7
$\text{Sn}(\text{HS}_2\text{O}_5)_4$	4 1 0	9 6
$\text{Sn}(\text{HS}_2\text{O}_2)_4$	4 3 9	9 4
$\text{Sn}(\text{HS}_2\text{O}_4)_4$	4 0 3	9 5
$\text{Sn}(\text{HSO}_2)_4$	4 7 0	9 0
$\text{Sn}(\text{HSO}_4)_2$	4 8 6	9 3
$\text{Sn}(\text{HSO}_3)_2$	4 9 6	8 8
$\text{Sn}(\text{HS}_2\text{O}_7)_2$	4 5 0	9 2
$\text{Sn}(\text{HSO}_5)_2$	4 5 7	9 1

Table 10

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
SnS <sub>2</sub> O <sub>8</sub>	4 6 0	8 6
SnS <sub>2</sub> O <sub>3</sub>	5 0 5	7 9
SnS <sub>2</sub> O <sub>6</sub>	4 7 6	8 5
SnS <sub>2</sub> O <sub>5</sub>	4 8 3	8 5
SnS <sub>2</sub> O <sub>2</sub>	5 3 6	8 0
SnS <sub>2</sub> O <sub>4</sub>	4 9 7	8 1
SnSO <sub>2</sub>	5 4 5	7 9
Si(SO <sub>4</sub> ) <sub>2</sub>	3 9 5	8 5
Si(SO <sub>3</sub> ) <sub>2</sub>	4 1 1	8 2
Si(S <sub>2</sub> O <sub>7</sub> ) <sub>2</sub>	3 4 1	8 7
Si(SO <sub>5</sub> ) <sub>2</sub>	3 6 2	8 5
Si(S <sub>2</sub> O <sub>6</sub> ) <sub>2</sub>	3 2 2	8 7
Si(S <sub>2</sub> O <sub>3</sub> ) <sub>2</sub>	3 7 5	8 4
Si(S <sub>2</sub> O <sub>6</sub> ) <sub>2</sub>	3 3 2	8 5
Si(S <sub>2</sub> O <sub>5</sub> ) <sub>2</sub>	3 4 3	8 4
Si(S <sub>2</sub> O <sub>2</sub> ) <sub>2</sub>	3 7 8	8 2
Si(S <sub>2</sub> O <sub>4</sub> ) <sub>2</sub>	3 5 0	8 5
Si(SO <sub>2</sub> ) <sub>2</sub>	4 2 1	8 3
PbSO <sub>4</sub>	4 5 2	8 4
PbSO <sub>3</sub>	4 7 2	8 3
PbS <sub>2</sub> O <sub>7</sub>	4 0 5	8 6
PbSO <sub>5</sub>	4 3 2	8 5
PbS <sub>2</sub> O <sub>6</sub>	4 0 0	8 6
PbS <sub>2</sub> O <sub>3</sub>	4 4 1	8 4
PbS <sub>2</sub> O <sub>6</sub>	4 1 1	8 5
PbS <sub>2</sub> O <sub>5</sub>	4 1 9	8 5
PbS <sub>2</sub> O <sub>2</sub>	4 4 5	8 2
PbS <sub>2</sub> O <sub>4</sub>	4 1 2	8 4
Sn(HS <sub>2</sub> O <sub>8</sub> ) <sub>2</sub>	4 2 6	9 3
Sn(HS <sub>2</sub> O <sub>3</sub> ) <sub>2</sub>	4 7 2	9 1
Sn(HS <sub>2</sub> O <sub>6</sub> ) <sub>2</sub>	4 3 6	9 4
Sn(HS <sub>2</sub> O <sub>5</sub> ) <sub>2</sub>	4 4 0	9 4
Sn(HS <sub>2</sub> O <sub>2</sub> ) <sub>2</sub>	4 7 1	9 1
Sn(HS <sub>2</sub> O <sub>4</sub> ) <sub>2</sub>	4 4 6	9 3
Sn(HSO <sub>2</sub> ) <sub>2</sub>	4 9 2	9 0
Si(HSO <sub>4</sub> ) <sub>4</sub>	3 6 2	9 3
Si(HSO <sub>3</sub> ) <sub>4</sub>	3 7 1	9 1
Si(HS <sub>2</sub> O <sub>7</sub> ) <sub>4</sub>	3 1 2	9 4
Si(HSO <sub>5</sub> ) <sub>4</sub>	3 3 5	9 5
Si(HS <sub>2</sub> O <sub>6</sub> ) <sub>4</sub>	2 9 4	9 6

Table 10-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{Si}(\text{HS}_2\text{O}_3)_4$	341	93
$\text{Si}(\text{HS}_2\text{O}_6)_4$	309	95
$\text{Si}(\text{HS}_2\text{O}_5)_4$	312	94
$\text{Si}(\text{HS}_2\text{O}_2)_4$	340	92
$\text{Si}(\text{HS}_2\text{O}_4)_4$	318	93
$\text{Si}(\text{HSO}_2)_4$	390	90
$\text{Pb}(\text{HSO}_4)_2$	415	92
$\text{Pb}(\text{HSO}_3)_2$	426	91
$\text{Pb}(\text{HS}_2\text{O}_7)_2$	386	95
$\text{Pb}(\text{HSO}_5)_2$	403	94
$\text{Pb}(\text{HS}_2\text{O}_8)_2$	376	95
$\text{Pb}(\text{HS}_2\text{O}_3)_2$	411	94
$\text{Pb}(\text{HS}_2\text{O}_6)_2$	389	96
$\text{Pb}(\text{HS}_2\text{O}_5)_2$	399	95
$\text{Pb}(\text{HS}_2\text{O}_2)_2$	419	91
$\text{Pb}(\text{HS}_2\text{O}_4)_2$	391	93

Table 11

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{PbSO}_2$	475	81
$\text{CdSO}_4$	414	79
$\text{CdSO}_3$	426	78
$\text{CdS}_2\text{O}_7$	378	81
$\text{CdSO}_5$	404	82
$\text{CdS}_2\text{O}_8$	369	84
$\text{CdS}_2\text{O}_3$	410	78
$\text{CdS}_2\text{O}_6$	398	79
$\text{CdS}_2\text{O}_5$	401	80
$\text{CdS}_2\text{O}_2$	410	78
$\text{CdS}_2\text{O}_4$	389	82
$\text{CdSO}_2$	420	76
$\text{Bi}_2(\text{SO}_4)_3$	364	76
$\text{Bi}_2(\text{SO}_3)_3$	381	75
$\text{Bi}_2(\text{S}_2\text{O}_7)_3$	324	79
$\text{Bi}_2(\text{SO}_5)_3$	348	78
$\text{Bi}_2(\text{S}_2\text{O}_8)_3$	315	81



Table 11-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{Bi}_2(\text{S}_2\text{O}_3)_3$	346	78
$\text{Bi}_2(\text{S}_2\text{O}_6)_3$	329	78
$\text{Bi}_2(\text{S}_2\text{O}_5)_3$	347	76
$\text{Bi}_2(\text{S}_2\text{O}_2)_3$	352	75
$\text{Bi}_2(\text{S}_2\text{O}_4)_3$	333	79
$\text{Bi}_2(\text{SO}_2)_3$	379	75
$\text{In}_2(\text{SO}_4)_3$	444	83
$\text{In}_2(\text{SO}_3)_3$	459	81
$\text{In}_2(\text{S}_2\text{O}_7)_3$	398	86
$\text{In}_2(\text{SO}_5)_3$	421	83
$\text{In}_2(\text{S}_2\text{O}_8)_3$	389	85
$\text{Pb}(\text{HSO}_2)_2$	435	91
$\text{Cd}(\text{HSO}_4)_2$	379	89
$\text{Cd}(\text{HSO}_3)_2$	398	88
$\text{Cd}(\text{HS}_2\text{O}_7)_2$	346	92
$\text{Cd}(\text{HSO}_5)_2$	382	93
$\text{Cd}(\text{HS}_2\text{O}_8)_2$	341	93
$\text{Cd}(\text{HS}_2\text{O}_3)_2$	379	90
$\text{Cd}(\text{HS}_2\text{O}_6)_2$	370	91
$\text{Cd}(\text{HS}_2\text{O}_5)_2$	374	93
$\text{Cd}(\text{HS}_2\text{O}_2)_2$	379	89
$\text{Cd}(\text{HS}_2\text{O}_4)_2$	365	93
$\text{Cd}(\text{HSO}_2)_2$	391	89
$\text{Bi}(\text{HSO}_4)_3$	337	87
$\text{Bi}(\text{HSO}_3)_3$	349	86
$\text{Bi}(\text{HS}_2\text{O}_7)_3$	298	87
$\text{Bi}(\text{HSO}_5)_3$	315	86
$\text{Bi}(\text{HS}_2\text{O}_8)_3$	276	90
$\text{Bi}(\text{HS}_2\text{O}_3)_3$	313	85
$\text{Bi}(\text{HS}_2\text{O}_6)_3$	298	86
$\text{Bi}(\text{HS}_2\text{O}_5)_3$	313	87
$\text{Bi}(\text{HS}_2\text{O}_2)_3$	321	84
$\text{Bi}(\text{HS}_2\text{O}_4)_3$	303	88
$\text{Bi}(\text{HSO}_2)_3$	336	86
$\text{In}(\text{HSO}_4)_3$	416	92
$\text{In}(\text{HSO}_3)_3$	420	91
$\text{In}(\text{HS}_2\text{O}_7)_3$	367	95
$\text{In}(\text{HSO}_5)_3$	390	94
$\text{In}(\text{HS}_2\text{O}_8)_3$	374	96

Table 12

	Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
5	$\text{In}_2(\text{S}_2\text{O}_3)_3$	432	84
	$\text{In}_2(\text{S}_2\text{O}_6)_3$	419	85
	$\text{In}_2(\text{S}_2\text{O}_5)_3$	416	85
10	$\text{In}_2(\text{S}_2\text{O}_2)_3$	432	83
	$\text{In}_2(\text{S}_2\text{O}_4)_3$	398	86
	$\text{In}_2(\text{SO}_2)_3$	456	81
	$\text{ZnSO}_4$	362	75
	$\text{ZnSO}_3$	379	73
15	$\text{ZnS}_2\text{O}_7$	334	76
	$\text{ZnSO}_5$	342	75
	$\text{ZnS}_2\text{O}_8$	320	76
	$\text{ZnS}_2\text{O}_3$	342	76
	$\text{ZnS}_2\text{O}_6$	320	76
20	$\text{ZnS}_2\text{O}_5$	333	75
	$\text{ZnS}_2\text{O}_2$	354	74
	$\text{ZnS}_2\text{O}_4$	321	76
	$\text{ZnSO}_2$	382	73
25	$\text{MgSO}_4$	333	81
	$\text{MgSO}_3$	352	79
	$\text{MgS}_2\text{O}_7$	298	84
	$\text{MgSO}_5$	320	82
	$\text{MgS}_2\text{O}_8$	302	83
30	$\text{MgS}_2\text{O}_3$	325	81
	$\text{MgS}_2\text{O}_6$	300	83
	$\text{MgS}_2\text{O}_5$	311	82
	$\text{MgS}_2\text{O}_2$	328	82
	$\text{MgS}_2\text{O}_4$	305	83
35	$\text{MgSO}_2$	342	79
	$\text{In}(\text{HS}_2\text{O}_3)_3$	400	95
	$\text{In}(\text{HS}_2\text{O}_6)_3$	381	95
	$\text{In}(\text{HS}_2\text{O}_5)_3$	390	95
40	$\text{In}(\text{HS}_2\text{O}_2)_3$	402	91
	$\text{In}(\text{HS}_2\text{O}_4)_3$	370	95
	$\text{In}(\text{HSO}_2)_3$	420	92
	$\text{Zn}(\text{HSO}_4)_2$	333	85
	$\text{Zn}(\text{HSO}_3)_2$	342	84
45	$\text{Zn}(\text{HS}_2\text{O}_7)_2$	300	87
	$\text{Zn}(\text{HSO}_5)_2$	312	86
	$\text{Zn}(\text{HS}_2\text{O}_8)_2$	294	85
	$\text{Zn}(\text{HS}_2\text{O}_3)_2$	310	85
50	$\text{Zn}(\text{HS}_2\text{O}_6)_2$	300	84
	$\text{Zn}(\text{HS}_2\text{O}_5)_2$	310	86
	$\text{Zn}(\text{HS}_2\text{O}_2)_2$	325	84

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Table 12-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
Zn(HS <sub>2</sub> O <sub>4</sub> ) <sub>2</sub>	290	86
Zn(HSO <sub>2</sub> ) <sub>2</sub>	341	84
Mg(HSO <sub>4</sub> ) <sub>2</sub>	312	91
Mg(HSO <sub>3</sub> ) <sub>2</sub>	330	89
Mg(HS <sub>2</sub> O <sub>7</sub> ) <sub>2</sub>	271	93
Mg(HSO <sub>5</sub> ) <sub>2</sub>	294	92
Mg(HS <sub>2</sub> O <sub>8</sub> ) <sub>2</sub>	279	93
Mg(HS <sub>2</sub> O <sub>3</sub> ) <sub>2</sub>	293	92
Mg(HS <sub>2</sub> O <sub>6</sub> ) <sub>2</sub>	276	94
Mg(HS <sub>2</sub> O <sub>5</sub> ) <sub>2</sub>	288	92
Mg(HS <sub>2</sub> O <sub>2</sub> ) <sub>2</sub>	296	93
Mg(HS <sub>2</sub> O <sub>4</sub> ) <sub>2</sub>	276	94
Mg(HSO <sub>2</sub> ) <sub>2</sub>	302	90

Table 13

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
Ga <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	364	76
Ga <sub>2</sub> (SO <sub>3</sub> ) <sub>3</sub>	382	74
Ga <sub>2</sub> (S <sub>2</sub> O <sub>7</sub> ) <sub>3</sub>	321	79
Ga <sub>2</sub> (SO <sub>5</sub> ) <sub>3</sub>	352	75
Ga <sub>2</sub> (S <sub>2</sub> O <sub>8</sub> ) <sub>3</sub>	312	77
Ga <sub>2</sub> (S <sub>2</sub> O <sub>3</sub> ) <sub>3</sub>	352	75
Ga <sub>2</sub> (S <sub>2</sub> O <sub>6</sub> ) <sub>3</sub>	333	76
Ga <sub>2</sub> (S <sub>2</sub> O <sub>5</sub> ) <sub>3</sub>	342	75
Ga <sub>2</sub> (S <sub>2</sub> O <sub>2</sub> ) <sub>3</sub>	354	74
Ga <sub>2</sub> (S <sub>2</sub> O <sub>4</sub> ) <sub>3</sub>	326	76
Ga <sub>2</sub> (SO <sub>2</sub> ) <sub>3</sub>	375	73
Ge(SO <sub>4</sub> ) <sub>2</sub>	431	78
Ge(SO <sub>3</sub> ) <sub>2</sub>	449	75
Ge(S <sub>2</sub> O <sub>7</sub> ) <sub>2</sub>	395	81
Ge(SO <sub>5</sub> ) <sub>2</sub>	423	78
Ge(S <sub>2</sub> O <sub>8</sub> ) <sub>2</sub>	386	81
Ge(S <sub>2</sub> O <sub>3</sub> ) <sub>2</sub>	425	77
Ge(S <sub>2</sub> O <sub>6</sub> ) <sub>2</sub>	401	80

Table 13-continued

	Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
5	$\text{Ge}(\text{S}_2\text{O}_5)_2$	4 0 8	7.9
	$\text{Ge}(\text{S}_2\text{O}_2)_2$	4 2 0	7.9
10	$\text{Ge}(\text{S}_2\text{O}_4)_2$	3 9 0	8.2
	$\text{Ge}(\text{SO}_2)_2$	4 3 5	7.7
	$\text{Cr}_2(\text{SO}_4)_3$	3 5 3	8.1
	$\text{Cr}_2(\text{SO}_3)_3$	3 6 9	8.0
15	$\text{W}(\text{SeO}_4)_2$	2 9 8	7.9
	$\text{CoSO}_4$	3 5 2	8.2
	$\text{CoSO}_3$	3 6 2	8.0
	$\text{NiSO}_4$	3 4 9	8.1
20	$\text{Ga}(\text{HSO}_4)_3$	3 3 9	8.6
	$\text{Ga}(\text{HSO}_3)_3$	3 5 2	8.5
	$\text{Ga}(\text{HS}_2\text{O}_7)_3$	3 0 1	8.8
	$\text{Ga}(\text{HSO}_5)_3$	3 1 5	8.4
	$\text{Ga}(\text{HS}_2\text{O}_8)_3$	2 9 4	8.6
25	$\text{Ga}(\text{HS}_2\text{O}_3)_3$	3 2 1	8.7
	$\text{Ga}(\text{HS}_2\text{O}_6)_3$	3 0 3	8.7
	$\text{Ga}(\text{HS}_2\text{O}_5)_3$	3 1 8	8.6
	$\text{Ga}(\text{HS}_2\text{O}_2)_3$	3 2 1	8.6
30	$\text{Ga}(\text{HS}_2\text{O}_4)_3$	2 9 6	8.4
	$\text{Ga}(\text{HSO}_2)_3$	3 4 8	8.4
	$\text{Ge}(\text{HSO}_4)_4$	4 1 2	8.9
	$\text{Ge}(\text{HSO}_3)_4$	4 2 1	8.6
35	$\text{Ge}(\text{HS}_2\text{O}_7)_4$	3 7 0	9.2
	$\text{Ge}(\text{HSO}_5)_4$	3 9 6	9.0
	$\text{Ge}(\text{HS}_2\text{O}_8)_4$	3 5 6	9.3
	$\text{Ge}(\text{HS}_2\text{O}_3)_4$	3 8 7	8.5
40	$\text{Ge}(\text{HS}_2\text{O}_6)_4$	3 7 4	8.8
	$\text{Ge}(\text{HS}_2\text{O}_5)_4$	3 7 3	8.7
	$\text{Ge}(\text{HS}_2\text{O}_2)_4$	3 9 5	8.9
	$\text{Ge}(\text{HS}_2\text{O}_4)_4$	3 6 5	9.3
45	$\text{Ge}(\text{HSO}_2)_4$	4 0 2	8.9
	$\text{Cr}(\text{HSO}_4)_3$	3 2 5	9.2
	$\text{Cr}(\text{HSO}_3)_3$	3 4 1	9.0
	$\text{W}(\text{HSO}_4)_4$	2 7 5	8.9
50	$\text{Co}(\text{HSO}_4)_2$	3 2 1	9.2
	$\text{Co}(\text{HSO}_3)_2$	3 2 9	9.0
	$\text{Ni}(\text{HSO}_4)_2$	3 1 9	9.0

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Table 14

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
NiSO <sub>3</sub>	354	79
CuSO <sub>4</sub>	326	82
CuSO <sub>3</sub>	340	80
Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	315	83
Mo <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	324	84
VSO <sub>4</sub>	306	83
MnSO <sub>4</sub>	345	82
MnSO <sub>3</sub>	356	80
FeSO <sub>4</sub>	354	81
FeSO <sub>3</sub>	362	78
Nb <sub>2</sub> (SO <sub>4</sub> ) <sub>5</sub>	257	82
CaSO <sub>4</sub>	398	78
CaSO <sub>3</sub>	405	76
SrSO <sub>4</sub>	398	78
SrSO <sub>3</sub>	405	76
BaSO <sub>4</sub>	375	79
BaSO <sub>3</sub>	386	78
Ni(HSO <sub>3</sub> ) <sub>2</sub>	326	88
Cu(HSO <sub>4</sub> ) <sub>2</sub>	301	93
Cu(HSO <sub>3</sub> ) <sub>2</sub>	319	91
Ti(HSO <sub>4</sub> ) <sub>3</sub>	284	90
Mo(HSO <sub>4</sub> ) <sub>3</sub>	299	92
V(HSO <sub>4</sub> ) <sub>2</sub>	274	92
Mn(HSO <sub>4</sub> ) <sub>2</sub>	315	93
Mn(HSO <sub>3</sub> ) <sub>2</sub>	320	90
Fe(HSO <sub>4</sub> ) <sub>2</sub>	327	91
Fe(HSO <sub>3</sub> ) <sub>2</sub>	333	89
Nb(HSO <sub>4</sub> ) <sub>5</sub>	229	90
Ca(HSO <sub>4</sub> ) <sub>2</sub>	375	87
Ca(HSO <sub>3</sub> ) <sub>2</sub>	381	85
Sr(HSO <sub>4</sub> ) <sub>2</sub>	375	87
Sr(HSO <sub>3</sub> ) <sub>2</sub>	381	85
Ba(HSO <sub>4</sub> ) <sub>2</sub>	352	87
Ba(HSO <sub>3</sub> ) <sub>2</sub>	360	86

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	Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
5	Mg <sub>0.1</sub> Sn <sub>0.9</sub> SO <sub>4</sub>	503	84
	Sr <sub>0.1</sub> Sn <sub>0.9</sub> SO <sub>4</sub>	503	84
10	Ca <sub>0.1</sub> Sn <sub>0.9</sub> SO <sub>4</sub>	503	84
	Zn <sub>0.1</sub> Sn <sub>0.9</sub> SO <sub>4</sub>	500	85
	Ni <sub>0.1</sub> Sn <sub>0.9</sub> SO <sub>4</sub>	495	84
	Fe <sub>0.1</sub> Sn <sub>0.9</sub> SO <sub>4</sub>	492	86
	Co <sub>0.1</sub> Sn <sub>0.9</sub> SO <sub>4</sub>	489	87
15	Mn <sub>0.1</sub> Sn <sub>0.9</sub> SO <sub>4</sub>	482	86
	Cu <sub>0.1</sub> Sn <sub>0.9</sub> SO <sub>4</sub>	485	85
	Mo <sub>0.1</sub> Sn <sub>0.9</sub> SO <sub>4</sub>	476	84
	V <sub>0.1</sub> Sn <sub>0.9</sub> SO <sub>4</sub>	473	86
20	W <sub>0.1</sub> Sn <sub>0.9</sub> SO <sub>4</sub>	459	83
	Cr <sub>0.2</sub> Sn <sub>0.7</sub> SO <sub>4</sub>	476	84
	Mo <sub>0.2</sub> Sn <sub>0.7</sub> SO <sub>4</sub>	476	85
	Mg <sub>0.1</sub> Pb <sub>0.9</sub> SO <sub>4</sub>	420	86
	Sr <sub>0.1</sub> Pb <sub>0.9</sub> SO <sub>4</sub>	420	86
25	Ca <sub>0.1</sub> Pb <sub>0.9</sub> SO <sub>4</sub>	420	86
	Zn <sub>0.1</sub> Pb <sub>0.9</sub> SO <sub>4</sub>	421	87
	Ni <sub>0.1</sub> Pb <sub>0.9</sub> SO <sub>4</sub>	415	86
	Fe <sub>0.1</sub> Pb <sub>0.9</sub> SO <sub>4</sub>	410	87
30	Co <sub>0.1</sub> Pb <sub>0.9</sub> SO <sub>4</sub>	416	88
	Mn <sub>0.1</sub> Pb <sub>0.9</sub> SO <sub>4</sub>	408	86
	Cu <sub>0.1</sub> Pb <sub>0.9</sub> SO <sub>4</sub>	406	87
	Mo <sub>0.1</sub> Pb <sub>0.9</sub> SO <sub>4</sub>	398	85
35	V <sub>0.1</sub> Pb <sub>0.9</sub> SO <sub>4</sub>	387	85
	W <sub>0.1</sub> Pb <sub>0.9</sub> SO <sub>4</sub>	376	85
	Cr <sub>0.2</sub> Pb <sub>0.7</sub> SO <sub>4</sub>	387	84
	Mo <sub>0.2</sub> Pb <sub>0.7</sub> SO <sub>4</sub>	389	85
40	Mg <sub>0.1</sub> Sn <sub>0.9</sub> (HSO <sub>4</sub> ) <sub>2</sub>	481	94
	Sr <sub>0.1</sub> Sn <sub>0.9</sub> (HSO <sub>4</sub> ) <sub>2</sub>	481	94
	Ca <sub>0.1</sub> Sn <sub>0.9</sub> (HSO <sub>4</sub> ) <sub>2</sub>	481	94
	Zn <sub>0.1</sub> Sn <sub>0.9</sub> (HSO <sub>4</sub> ) <sub>2</sub>	479	95
	Ni <sub>0.1</sub> Sn <sub>0.9</sub> (HSO <sub>4</sub> ) <sub>2</sub>	470	95
45	Fe <sub>0.1</sub> Sn <sub>0.9</sub> (HSO <sub>4</sub> ) <sub>2</sub>	476	95
	Co <sub>0.1</sub> Sn <sub>0.9</sub> (HSO <sub>4</sub> ) <sub>2</sub>	469	94
	Mn <sub>0.1</sub> Sn <sub>0.9</sub> (HSO <sub>4</sub> ) <sub>2</sub>	465	96
	Cu <sub>0.1</sub> Sn <sub>0.9</sub> (HSO <sub>4</sub> ) <sub>2</sub>	462	94
	Mo <sub>0.1</sub> Sn <sub>0.9</sub> (HSO <sub>4</sub> ) <sub>2</sub>	459	95
50	V <sub>0.1</sub> Sn <sub>0.9</sub> (HSO <sub>4</sub> ) <sub>2</sub>	451	95
	W <sub>0.1</sub> Sn <sub>0.9</sub> (HSO <sub>4</sub> ) <sub>2</sub>	432	94
	Cr <sub>0.2</sub> Sn <sub>0.7</sub> (HSO <sub>4</sub> ) <sub>2</sub>	455	94

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Table 15-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{Mo}_{0.2}\text{Sn}_{0.7}(\text{HSO}_4)_2$	452	95
$\text{Mg}_{0.1}\text{Pb}_{0.9}(\text{HSO}_4)_2$	394	95
$\text{Sr}_{0.1}\text{Pb}_{0.9}(\text{HSO}_4)_2$	394	95
$\text{Ca}_{0.1}\text{Pb}_{0.9}(\text{HSO}_4)_2$	394	95
$\text{Zn}_{0.1}\text{Pb}_{0.9}(\text{HSO}_4)_2$	394	94
$\text{Ni}_{0.1}\text{Pb}_{0.9}(\text{HSO}_4)_2$	384	97
$\text{Fe}_{0.1}\text{Pb}_{0.9}(\text{HSO}_4)_2$	381	95
$\text{Co}_{0.1}\text{Pb}_{0.9}(\text{HSO}_4)_2$	384	96
$\text{Mn}_{0.1}\text{Pb}_{0.9}(\text{HSO}_4)_2$	381	95
$\text{Cu}_{0.1}\text{Pb}_{0.9}(\text{HSO}_4)_2$	386	96
$\text{Mo}_{0.1}\text{Pb}_{0.9}(\text{HSO}_4)_2$	370	95
$\text{V}_{0.1}\text{Pb}_{0.9}(\text{HSO}_4)_2$	368	94
$\text{W}_{0.1}\text{Pb}_{0.9}(\text{HSO}_4)_2$	359	95
$\text{Cr}_{0.2}\text{Pb}_{0.7}(\text{HSO}_4)_2$	364	94
$\text{Mo}_{0.2}\text{Pb}_{0.7}(\text{HSO}_4)_2$	368	94

Table 16

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$(\text{Mg}_{0.3}\text{In}_{0.8})_2(\text{SO}_4)_3$	410	85
$(\text{Zn}_{0.3}\text{In}_{0.8})_2(\text{SO}_4)_3$	406	86
$(\text{Ni}_{0.3}\text{In}_{0.8})_2(\text{SO}_4)_3$	398	86
$(\text{Co}_{0.3}\text{Bi}_{0.8})_2(\text{SO}_4)_3$	333	80
$(\text{Fe}_{0.3}\text{Bi}_{0.8})_2(\text{SO}_4)_3$	325	82
$(\text{Mn}_{0.3}\text{Bi}_{0.8})_2(\text{SO}_4)_3$	330	80
$\text{Sn}(\text{SO}_4)_{0.5}(\text{HSO}_4)$	498	90
$\text{Pb}(\text{SO}_4)_{0.5}(\text{HSO}_4)$	425	90
$\text{In}_2(\text{SO}_4)_{2.5}(\text{HSO}_4)$	425	90
$\text{Bi}_2(\text{SO}_4)_{2.5}(\text{HSO}_4)$	343	84
$\text{Co}_{0.3}\text{In}_{0.8}(\text{HSO}_4)_3$	379	94
$\text{Fe}_{0.3}\text{In}_{0.8}(\text{HSO}_4)_3$	370	95
$\text{Mn}_{0.3}\text{In}_{0.8}(\text{HSO}_4)_3$	368	95
$\text{Mg}_{0.3}\text{Bi}_{0.8}(\text{HSO}_4)_3$	298	90
$\text{Zn}_{0.3}\text{Bi}_{0.8}(\text{HSO}_4)_3$	289	89
$\text{Ni}_{0.3}\text{Bi}_{0.8}(\text{HSO}_4)_3$	295	91
$\text{Sn}(\text{SO}_4)_{0.9}(\text{HSO}_4)_{0.2}$	519	86

Table 16 (continued)

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{Pb}(\text{SO}_4)_{0.9}(\text{HSO}_4)_{0.2}$	438	87
$\text{In}_2(\text{SO}_4)_{2.9}(\text{HSO}_4)_{0.2}$	438	86
$\text{Bi}_2(\text{SO}_4)_{2.9}(\text{HSO}_4)_{0.2}$	350	80

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 4.

The batteries using the metal or semi-metal sulfate, sulfite, disulfate, peroxomonosulfate, peroxodisulfate, thiosulfate, disulfite, thiosulfite, hydrogensulfate, thionate, or sulfoxylate of Example 4 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides. Especially the use of hydrogensulfates has remarkably improved the cycle characteristics.

#### Example 5

The electrode characteristics of various salts of oxo-acids of selenium specified in Tables 17 through 20 and used as the anode active material were evaluated in Example 5.

Tables 17 through 20 show the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.



Table 17

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Al_2(SeO_4)_3$	362	83
$Al_2(SeO_3)_3$	387	80
$Sn(SeO_4)_2$	462	84
$Sn(SeO_3)_2$	483	81
$SnSeO_4$	512	83
$SnSeO_3$	521	80
$Sn_2SeO_5$	534	79
$Si(SeO_4)_2$	364	84
$Si(SeO_3)_2$	379	80
$PbSeO_4$	432	85
$PbSeO_3$	445	82
$Pb_2SeO_5$	498	80
$CdSeO_4$	386	80
$CdSeO_3$	399	78
$Bi_2(SeO_4)_3$	339	77
$Bi_2(SeO_3)_3$	349	72
$In_2(SeO_4)_3$	421	85
$In_2(SeO_3)_3$	438	83
$ZnSeO_4$	339	74
$ZnSeO_3$	348	70
$MgSeO_4$	310	82
$MgSeO_3$	321	79
$Ga_2(SeO_4)_3$	339	75
$Ga_2(SeO_3)_3$	349	73
$Ge(SeO_4)_2$	405	77
$Ge(SeO_3)_2$	420	72
$Al(HSeO_4)_3$	341	92
$Al(HSeO_3)_3$	367	89
$Sn(HSeO_4)_4$	442	92
$Sn(HSeO_3)_4$	462	93
$Sn(HSeO_4)_2$	489	94
$Sn(HSeO_3)_2$	501	90
$SnSeO_5$	508	84
$Si(HSeO_4)_4$	342	92
$Si(HSeO_3)_4$	347	90
$Pb(HSeO_4)_2$	412	93
$Pb(HSeO_3)_2$	421	92
$PbSeO_5$	425	85
$Cd(HSeO_4)_2$	364	90
$Cd(HSeO_3)_2$	374	88
$Bi(HSeO_4)_3$	314	89
$Bi(HSeO_3)_3$	321	86

Table 17-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
In(HSeO <sub>4</sub> ) <sub>3</sub>	3 9 7	9 4
In(HSeO <sub>3</sub> ) <sub>3</sub>	4 0 9	9 3
Zn(HSeO <sub>4</sub> ) <sub>2</sub>	3 1 5	8 5
Zn(HSeO <sub>3</sub> ) <sub>2</sub>	3 2 0	8 3
Mg(HSeO <sub>4</sub> ) <sub>2</sub>	2 8 9	9 2
Mg(HSeO <sub>3</sub> ) <sub>2</sub>	3 0 1	8 7
Ga(HSeO <sub>4</sub> ) <sub>3</sub>	3 1 4	8 6
Ga(HSeO <sub>3</sub> ) <sub>3</sub>	3 2 4	8 4
Ge(HSeO <sub>4</sub> ) <sub>4</sub>	3 8 5	8 6
Ge(HSeO <sub>3</sub> ) <sub>4</sub>	3 9 6	8 3

Table 18

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
Cr <sub>2</sub> (SeO <sub>4</sub> ) <sub>3</sub>	3 2 1	7 5
Cr <sub>2</sub> (SeO <sub>3</sub> ) <sub>3</sub>	3 3 1	7 6
W(SeO <sub>4</sub> ) <sub>2</sub>	2 5 7	7 2
CoSeO <sub>4</sub>	2 8 6	7 3
CoSeO <sub>3</sub>	2 9 7	7 6
NiSeO <sub>4</sub>	2 8 6	7 6
NiSeO <sub>3</sub>	2 9 9	7 6
CuSeO <sub>4</sub>	2 8 7	7 3
CuSeO <sub>3</sub>	2 8 9	7 4
Ti <sub>2</sub> (SeO <sub>4</sub> ) <sub>3</sub>	2 5 3	7 7
Mo <sub>2</sub> (SeO <sub>4</sub> ) <sub>3</sub>	2 2 3	7 3
VSeO <sub>4</sub>	2 8 2	7 9
MnSeO <sub>4</sub>	2 6 5	7 3
MnSeO <sub>3</sub>	2 7 6	7 5
FeSeO <sub>4</sub>	2 8 2	7 4
FeSeO <sub>3</sub>	2 9 3	7 5
Nb <sub>2</sub> (SeO <sub>4</sub> ) <sub>5</sub>	2 1 5	7 5
CaSeO <sub>4</sub>	3 2 1	7 4
CaSeO <sub>3</sub>	3 3 4	7 6
SrSeO <sub>3</sub>	3 3 4	7 6
BaSeO <sub>4</sub>	3 4 5	7 3
BaSeO <sub>3</sub>	3 5 3	7 4
Sb <sub>2</sub> (SeO <sub>4</sub> ) <sub>3</sub>	3 6 4	7 2

Table 18-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{Ir}_2(\text{SeO}_4)_3$	345	73
$\text{Cr}(\text{HSeO}_4)_3$	305	84
$\text{Cr}(\text{HSeO}_3)_3$	314	86
$\text{W}(\text{HSeO}_4)_4$	234	83
$\text{Co}(\text{HSeO}_4)_2$	261	82
$\text{Co}(\text{HSeO}_3)_2$	271	85
$\text{Ni}(\text{HSeO}_4)_2$	264	84
$\text{Ni}(\text{HSeO}_3)_2$	274	85
$\text{Cu}(\text{HSeO}_4)_2$	264	84
$\text{Cu}(\text{HSeO}_3)_2$	259	84
$\text{Ti}(\text{HSeO}_4)_3$	230	86
$\text{Mo}(\text{HSeO}_4)_3$	201	84
$\text{V}(\text{HSeO}_4)_2$	261	89
$\text{Mn}(\text{HSeO}_4)_2$	241	82
$\text{Mn}(\text{HSeO}_3)_2$	251	84
$\text{Fe}(\text{HSeO}_4)_2$	260	86
$\text{Fe}(\text{HSeO}_3)_2$	271	85
$\text{Nb}(\text{HSeO}_4)_5$	195	84
$\text{Ca}(\text{HSeO}_4)_2$	301	82
$\text{Ca}(\text{HSeO}_3)_2$	309	85
$\text{Sr}(\text{HSeO}_4)_2$	309	85
$\text{Ba}(\text{HSeO}_4)_2$	314	84
$\text{Ba}(\text{HSeO}_3)_2$	321	83
$\text{Sb}(\text{HSeO}_4)_3$	335	86
$\text{Ir}(\text{HSeO}_4)_3$	315	85

Table 19

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{MgO} \cdot \text{SnO}_2 \cdot \text{SeO}_4$	486	85
$\text{ZnO} \cdot \text{SnO}_2 \cdot \text{SeO}_4$	484	86
$\text{NiO} \cdot \text{SnO}_2 \cdot \text{SeO}_4$	472	85
$\text{FeO} \cdot \text{SnO}_2 \cdot \text{SeO}_4$	471	86
$\text{CoO} \cdot \text{SnO}_2 \cdot \text{SeO}_4$	476	87
$\text{MnO} \cdot \text{SnO}_2 \cdot \text{SeO}_4$	483	84
$\text{CuO} \cdot \text{SnO}_2 \cdot \text{SeO}_4$	475	85
$\text{MoO}_3 \cdot \text{SnO}_2 \cdot \text{SeO}_4$	465	86
$\text{VO}_2 \cdot \text{SnO}_2 \cdot \text{SeO}_4$	459	88
$\text{WO}_3 \cdot \text{SnO}_2 \cdot \text{SeO}_4$	443	88
$\text{CrO}_3 \cdot \text{SnO}_2 \cdot \text{SeO}_4$	433	86
$\text{CaO} \cdot \text{SnO}_2 \cdot \text{SeO}_4$	492	85

Table 19-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
SrO <sub>2</sub> ·SnO <sub>2</sub> ·SeO <sub>4</sub>	492	85
BaO <sub>2</sub> ·SnO <sub>2</sub> ·SeO <sub>4</sub>	475	86
MgO <sub>2</sub> ·PbO <sub>2</sub> ·SeO <sub>4</sub>	415	85
ZnO <sub>2</sub> ·PbO <sub>2</sub> ·SeO <sub>4</sub>	409	86
NiO <sub>2</sub> ·PbO <sub>2</sub> ·SeO <sub>4</sub>	414	87
FeO <sub>2</sub> ·PbO <sub>2</sub> ·SeO <sub>4</sub>	401	88
CoO <sub>2</sub> ·PbO <sub>2</sub> ·SeO <sub>4</sub>	405	86
MnO <sub>2</sub> ·PbO <sub>2</sub> ·SeO <sub>4</sub>	403	84
CuO <sub>2</sub> ·PbO <sub>2</sub> ·SeO <sub>4</sub>	402	85
MoO <sub>2</sub> ·PbO <sub>2</sub> ·SeO <sub>4</sub>	394	85
VO <sub>2</sub> ·PbO <sub>2</sub> ·SeO <sub>4</sub>	396	84
WO <sub>2</sub> ·PbO <sub>2</sub> ·SeO <sub>4</sub>	379	86
CrO <sub>2</sub> ·PbO <sub>2</sub> ·SeO <sub>4</sub>	368	85
CaO <sub>2</sub> ·PbO <sub>2</sub> ·SeO <sub>4</sub>	408	85
SrO <sub>2</sub> ·PbO <sub>2</sub> ·SeO <sub>4</sub>	408	85
BaO <sub>2</sub> ·PbO <sub>2</sub> ·SeO <sub>4</sub>	381	86
MgO <sub>2</sub> ·SnO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	453	94
ZnO <sub>2</sub> ·SnO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	461	96
NiO <sub>2</sub> ·SnO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	453	95
FeO <sub>2</sub> ·SnO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	449	94
CoO <sub>2</sub> ·SnO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	448	95
MnO <sub>2</sub> ·SnO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	457	92
CuO <sub>2</sub> ·SnO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	453	94
MoO <sub>2</sub> ·SnO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	441	95
VO <sub>2</sub> ·SnO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	432	97
WO <sub>2</sub> ·SnO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	420	96
CrO <sub>2</sub> ·SnO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	416	95
CaO <sub>2</sub> ·SnO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	470	95
SrO <sub>2</sub> ·SnO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	470	95
BaO <sub>2</sub> ·SnO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	448	94
MgO <sub>2</sub> ·PbO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	385	94
ZnO <sub>2</sub> ·PbO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	389	95
NiO <sub>2</sub> ·PbO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	391	96
FeO <sub>2</sub> ·PbO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	371	98
CoO <sub>2</sub> ·PbO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	379	95
MnO <sub>2</sub> ·PbO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	371	95
CuO <sub>2</sub> ·PbO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	376	96
MoO <sub>2</sub> ·PbO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	370	94
VO <sub>2</sub> ·PbO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	369	95
WO <sub>2</sub> ·PbO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	349	97
CrO <sub>2</sub> ·PbO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	333	96
CaO <sub>2</sub> ·PbO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	379	94
SrO <sub>2</sub> ·PbO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	379	94
BaO <sub>2</sub> ·PbO <sub>2</sub> ·(HSeO <sub>4</sub> ) <sub>2</sub>	353	96

Table 20

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$(\text{Mg}_{0.3}\text{In}_{0.8})_2(\text{SeO}_4)_3$	398	86
$(\text{Zn}_{0.3}\text{In}_{0.8})_2(\text{SeO}_4)_3$	387	87
$(\text{Ni}_{0.3}\text{In}_{0.8})_2(\text{SeO}_4)_3$	379	86
$(\text{Co}_{0.3}\text{Bi}_{0.8})_2(\text{SeO}_4)_3$	318	80
$(\text{Fe}_{0.3}\text{Bi}_{0.8})_2(\text{SeO}_4)_3$	310	82
$(\text{Mn}_{0.3}\text{Bi}_{0.8})_2(\text{SeO}_4)_3$	320	82
$\text{Co}_{0.3}\text{In}_{0.8}(\text{HSeO}_4)_3$	374	95
$\text{Fe}_{0.3}\text{In}_{0.8}(\text{HSeO}_4)_3$	361	98
$\text{Mn}_{0.3}\text{In}_{0.8}(\text{HSeO}_4)_3$	348	96
$\text{Mg}_{0.3}\text{Bi}_{0.8}(\text{HSeO}_4)_3$	279	91
$\text{Zn}_{0.3}\text{Bi}_{0.8}(\text{HSeO}_4)_3$	284	92
$\text{Ni}_{0.3}\text{Bi}_{0.8}(\text{HSeO}_4)_3$	298	93

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 5.

The batteries using the metal or semi-metal selenate, selenite, hydrogenselenate, or hydrogenselenite of Example 5 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides. Especially the use of hydrogenselenates and hydrogenselenites has remarkably improved the cycle characteristics.

#### Example 6

The electrode characteristics of various salts of oxo-acids of tellurium specified in Tables 21 through 23 and used as the anode active material were evaluated in Example 6.

Tables 21 through 23 show the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 21

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Al_2(TeO_4)_3$	346	82
$SnTeO_4$	426	84
$SnTe_3O_8$	385	87
$Sn_3TeO_8$	489	85
$Si(TeO_4)_2$	337	83
$PbTeO_4$	405	84
$PbTe_3O_8$	352	85
$Pb_3TeO_8$	453	82
$CdTeO_4$	354	79
$Bi_2(TeO_4)_3$	314	79
$Bi_2TeO_8$	345	77
$In_2(TeO_4)_3$	384	82
$In_2TeO_8$	405	80
$Sb_2TeO_8$	384	78
$Ir_2TeO_8$	351	78
$ZnTeO_4$	302	75
$MgTeO_4$	289	81
$Ga_2TeO_8$	314	74
$Ge(TeO_4)_2$	370	75
$Ti_2TeO_8$	221	78
$Cr_2TeO_8$	287	74
$NiTeO_4$	253	76
$FeTeO_4$	254	75
$MnTeO_4$	247	74
$CoTeO_4$	253	75
$VTeO_4$	241	76
$CuTeO_4$	251	75
$Al(HTeO_4)_3$	319	89
$Sn(HTeO_4)_2$	397	90
$SnH_4TeO_8$	359	95

Table 21-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
Sn <sub>2</sub> H <sub>2</sub> TeO <sub>6</sub>	459	94
Si(HTeO <sub>4</sub> ) <sub>4</sub>	307	93
Pb(HTeO <sub>4</sub> ) <sub>2</sub>	372	92
PbH <sub>4</sub> TeO <sub>6</sub>	321	94
Pb <sub>2</sub> H <sub>2</sub> TeO <sub>6</sub>	426	93
Cd(HTeO <sub>4</sub> ) <sub>2</sub>	320	90
Bi(HTeO <sub>4</sub> ) <sub>3</sub>	284	87
BiH <sub>3</sub> TeO <sub>6</sub>	314	87
In(HTeO <sub>4</sub> ) <sub>3</sub>	359	89
InH <sub>3</sub> TeO <sub>6</sub>	374	90
SbH <sub>3</sub> TeO <sub>6</sub>	352	89
IrH <sub>3</sub> TeO <sub>6</sub>	321	88
Zn(HTeO <sub>4</sub> ) <sub>2</sub>	275	86
Mg(HSeO <sub>4</sub> ) <sub>2</sub>	264	89
GaH <sub>3</sub> TeO <sub>6</sub>	275	86
Ge(HTeO <sub>4</sub> ) <sub>4</sub>	342	86
TiH <sub>3</sub> TeO <sub>6</sub>	198	87
CrH <sub>3</sub> TeO <sub>6</sub>	255	86
Ni(HTeO <sub>4</sub> ) <sub>2</sub>	234	87
Fe(HSeO <sub>4</sub> ) <sub>2</sub>	229	86
Mn(HTeO <sub>4</sub> ) <sub>2</sub>	219	85
Co(HSeO <sub>4</sub> ) <sub>2</sub>	218	85
V(HTeO <sub>4</sub> ) <sub>2</sub>	214	87
Cu(HTeO <sub>4</sub> ) <sub>2</sub>	216	85

Table 22

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
MoTeO <sub>4</sub>	234	73
W(TeO <sub>4</sub> ) <sub>2</sub>	215	73
CaTeO <sub>4</sub>	315	74
SrTeO <sub>4</sub>	315	74
BaTeO <sub>4</sub>	305	75
Mg <sub>0.1</sub> Sn <sub>0.9</sub> TeO <sub>4</sub>	402	86
Ca <sub>0.1</sub> Sn <sub>0.9</sub> TeO <sub>4</sub>	402	86
Sr <sub>0.1</sub> Sn <sub>0.9</sub> TeO <sub>4</sub>	402	86
Zn <sub>0.1</sub> Sn <sub>0.9</sub> TeO <sub>4</sub>	405	85
Ni <sub>0.1</sub> Sn <sub>0.9</sub> TeO <sub>4</sub>	400	86
Fe <sub>0.1</sub> Sn <sub>0.9</sub> TeO <sub>4</sub>	398	87
Co <sub>0.1</sub> Sn <sub>0.9</sub> TeO <sub>4</sub>	396	86
Mn <sub>0.1</sub> Sn <sub>0.9</sub> TeO <sub>4</sub>	389	85
Cu <sub>0.1</sub> Sn <sub>0.9</sub> TeO <sub>4</sub>	390	85
Mo <sub>0.1</sub> Sn <sub>0.9</sub> TeO <sub>4</sub>	379	87

Table 22-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
V <sub>2</sub> O <sub>5</sub> ·SnO <sub>2</sub> ·TeO <sub>4</sub>	378	88
W <sub>2</sub> O <sub>5</sub> ·SnO <sub>2</sub> ·TeO <sub>4</sub>	369	85
Cr <sub>2</sub> O <sub>3</sub> ·SnO <sub>2</sub> ·TeO <sub>4</sub>	374	86
MgO <sub>2</sub> ·PbO <sub>2</sub> ·TeO <sub>4</sub>	375	86
CaO <sub>2</sub> ·PbO <sub>2</sub> ·TeO <sub>4</sub>	375	86
SrO <sub>2</sub> ·PbO <sub>2</sub> ·TeO <sub>4</sub>	375	86
ZnO <sub>2</sub> ·PbO <sub>2</sub> ·TeO <sub>4</sub>	379	85
NiO <sub>2</sub> ·PbO <sub>2</sub> ·TeO <sub>4</sub>	370	87
FeO <sub>2</sub> ·PbO <sub>2</sub> ·TeO <sub>4</sub>	367	88
CoO <sub>2</sub> ·PbO <sub>2</sub> ·TeO <sub>4</sub>	368	87
MnO <sub>2</sub> ·PbO <sub>2</sub> ·TeO <sub>4</sub>	364	86
CuO <sub>2</sub> ·PbO <sub>2</sub> ·TeO <sub>4</sub>	362	87
MoO <sub>3</sub> ·PbO <sub>2</sub> ·TeO <sub>4</sub>	354	87
V <sub>2</sub> O <sub>5</sub> ·PbO <sub>2</sub> ·TeO <sub>4</sub>	352	86
W <sub>2</sub> O <sub>5</sub> ·PbO <sub>2</sub> ·TeO <sub>4</sub>	341	85
Mo(HTeO <sub>4</sub> ) <sub>2</sub>	215	81
W(HTeO <sub>4</sub> ) <sub>2</sub>	185	82
Ca(HTeO <sub>4</sub> ) <sub>2</sub>	289	84
Sr(HTeO <sub>4</sub> ) <sub>2</sub>	289	84
Ba(HTeO <sub>4</sub> ) <sub>2</sub>	279	83
MgO <sub>2</sub> ·SnO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	375	95
CaO <sub>2</sub> ·SnO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	375	95
SrO <sub>2</sub> ·SnO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	375	95
ZnO <sub>2</sub> ·SnO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	379	94
NiO <sub>2</sub> ·SnO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	374	95
FeO <sub>2</sub> ·SnO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	370	96
CoO <sub>2</sub> ·SnO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	375	95
MnO <sub>2</sub> ·SnO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	369	94
CuO <sub>2</sub> ·SnO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	371	94
MoO <sub>3</sub> ·SnO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	352	95
V <sub>2</sub> O <sub>5</sub> ·SnO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	349	97
W <sub>2</sub> O <sub>5</sub> ·SnO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	342	95
Cr <sub>2</sub> O <sub>3</sub> ·SnO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	344	94
MgO <sub>2</sub> ·PbO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	335	95
CaO <sub>2</sub> ·PbO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	335	95
SrO <sub>2</sub> ·PbO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	335	95
ZnO <sub>2</sub> ·PbO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	339	94
NiO <sub>2</sub> ·PbO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	348	95
FeO <sub>2</sub> ·PbO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	332	96
CoO <sub>2</sub> ·PbO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	321	95
MnO <sub>2</sub> ·PbO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	322	94
CuO <sub>2</sub> ·PbO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	337	95
MoO <sub>3</sub> ·PbO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	326	94
V <sub>2</sub> O <sub>5</sub> ·PbO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	322	95
W <sub>2</sub> O <sub>5</sub> ·PbO <sub>2</sub> ·(HTeO <sub>4</sub> ) <sub>2</sub>	320	96



Table 23

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{Cr}_{0.2}\text{Pb}_{0.7}\text{TeO}_4$	361	84
$(\text{Mg}_{0.3}\text{In}_{0.8})_2\text{TeO}_6$	374	82
$(\text{Zn}_{0.3}\text{In}_{0.8})_2\text{TeO}_6$	370	83
$(\text{Fe}_{0.3}\text{In}_{0.8})_2\text{TeO}_6$	364	84
$(\text{Mg}_{0.3}\text{Bi}_{0.8})_2\text{TeO}_6$	315	79
$(\text{Zn}_{0.3}\text{Bi}_{0.8})_2\text{TeO}_6$	318	80
$(\text{Fe}_{0.3}\text{Bi}_{0.8})_2\text{TeO}_6$	308	81
$\text{Cr}_{0.2}\text{Pb}_{0.7}(\text{HTeO}_4)_2$	337	93
$\text{Cr}_{0.3}\text{In}_{0.8}\text{H}_3\text{TeO}_6$	351	93
$\text{Ni}_{0.3}\text{In}_{0.8}\text{H}_3\text{TeO}_6$	341	92
$\text{Mn}_{0.3}\text{In}_{0.8}\text{H}_3\text{TeO}_6$	338	92
$\text{Co}_{0.3}\text{Bi}_{0.8}\text{H}_3\text{TeO}_6$	287	88
$\text{Ni}_{0.3}\text{Bi}_{0.8}\text{H}_3\text{TeO}_6$	286	90
$\text{Mn}_{0.3}\text{Bi}_{0.8}\text{H}_3\text{TeO}_6$	279	90

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 6.

The batteries using the metal or semi-metal tellurate or hydrogentellurate of Example 6 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides. Especially the use of hydrogentellurates has remarkably improved the cycle characteristics.

#### Example 7

The electrode characteristics of various metal and semi-metal hydrogenphosphates, phosphinates, and phosphonates specified in Tables 24 through 27 and used as the anode active material were evaluated in Example 7.

Tables 24 through 27 show the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 24

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{Al}(\text{PH}_2\text{O}_2)_3$	366	83
$\text{Al}_2(\text{PHO}_3)_3$	353	84
$\text{Al}_2(\text{HPO}_4)_3$	348	85
$\text{Al}(\text{H}_2\text{PO}_4)_3$	315	87
$\text{Sn}(\text{PH}_2\text{O}_2)_4$	412	88
$\text{Sn}(\text{PHO}_3)_2$	455	89
$\text{Sn}(\text{HPO}_4)_2$	452	88
$\text{Sn}(\text{H}_2\text{PO}_4)_4$	384	89
$\text{Sn}(\text{PH}_2\text{O}_2)_2$	452	82

Table 24 (continued)

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
SnPHO <sub>3</sub>	486	92
SnHPO <sub>4</sub>	485	95
Sn(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	402	86
Si(PH <sub>2</sub> O <sub>2</sub> ) <sub>4</sub>	304	85
Si(PO <sub>3</sub> ) <sub>2</sub>	332	86
Bi(PH <sub>2</sub> O <sub>2</sub> ) <sub>3</sub>	333	82
Bi <sub>2</sub> (PHO <sub>3</sub> ) <sub>3</sub>	345	83
Bi <sub>2</sub> (HPO <sub>4</sub> ) <sub>3</sub>	340	83
Bi(H <sub>2</sub> PO <sub>4</sub> ) <sub>3</sub>	324	85
In(PH <sub>2</sub> O <sub>2</sub> ) <sub>3</sub>	365	82
In <sub>2</sub> (PHO <sub>3</sub> ) <sub>3</sub>	380	81
In <sub>2</sub> (HPO <sub>4</sub> ) <sub>3</sub>	377	83
In(H <sub>2</sub> PO <sub>4</sub> ) <sub>3</sub>	333	86
Zn(PH <sub>2</sub> O <sub>2</sub> ) <sub>2</sub>	298	83
ZnPHO <sub>3</sub>	298	83
ZnHPO <sub>4</sub>	295	83
Zn(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	264	84
Mg(PH <sub>2</sub> O <sub>2</sub> ) <sub>2</sub>	281	84
MgPHO <sub>3</sub>	288	83

Table 25

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
Si(HPO <sub>4</sub> ) <sub>2</sub>	322	87
Si(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	285	88
Pb(PH <sub>2</sub> O <sub>2</sub> ) <sub>2</sub>	420	85
PbPHO <sub>3</sub>	425	85
PbHPO <sub>4</sub>	418	89
Pb(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	405	90
Cd(PH <sub>2</sub> O <sub>2</sub> ) <sub>2</sub>	380	82
CdPHO <sub>3</sub>	385	83
CdHPO <sub>4</sub>	384	83
Cd(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	375	86
Sb <sub>2</sub> (HPO <sub>4</sub> ) <sub>3</sub>	321	82
Ti <sub>2</sub> (HPO <sub>4</sub> ) <sub>3</sub>	275	84
V <sub>2</sub> (HPO <sub>4</sub> ) <sub>3</sub>	250	85

Table 25 (continued)

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{Cr}_2(\text{HPO}_4)_3$	284	84
$\text{Mn}_2(\text{HPO}_4)_3$	275	85
$\text{MgHPO}_4$	286	84
$\text{Mg}(\text{H}_2\text{PO}_4)_2$	267	87
$\text{Ga}(\text{PH}_2\text{O}_2)_3$	321	82
$\text{Ga}_2(\text{PHO}_3)_3$	335	83
$\text{Ga}_2(\text{HPO}_4)_3$	325	84
$\text{Ga}(\text{H}_2\text{PO}_4)_3$	305	86
$\text{Ge}(\text{PH}_2\text{O}_2)_4$	367	83
$\text{Ge}(\text{PHO}_3)_2$	382	84
$\text{Ge}(\text{HPO}_4)_2$	375	87
$\text{Ge}(\text{H}_2\text{PO}_4)_4$	342	89
$\text{Fe}_2(\text{HPO}_4)_3$	264	85
$\text{CoHPO}_4$	264	84
$\text{NiHPO}_4$	261	84
$\text{CuHPO}_4$	275	85

Table 26

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{SrHPO}_4$	332	85
$\text{Ca}_{0.2}\text{Sn}_{0.8}\text{HPO}_4$	451	88
$\text{Sr}_{0.2}\text{Sn}_{0.8}\text{HPO}_4$	451	88
$\text{Ba}_{0.2}\text{Sn}_{0.8}\text{HPO}_4$	432	89
$\text{Zn}_{0.2}\text{Sn}_{0.8}\text{HPO}_4$	437	92
$\text{Fe}_{0.2}\text{Sn}_{0.8}\text{HPO}_4$	441	91
$\text{Ni}_{0.2}\text{Sn}_{0.8}\text{HPO}_4$	438	92
$\text{Co}_{0.2}\text{Sn}_{0.8}\text{HPO}_4$	442	92
$\text{Mn}_{0.2}\text{Sn}_{0.8}\text{HPO}_4$	429	90
$\text{Ti}_{0.2}\text{Sn}_{0.7}\text{HPO}_4$	415	91
$\text{Cu}_{0.2}\text{Sn}_{0.8}\text{HPO}_4$	429	92
$\text{Cr}_{0.2}\text{Sn}_{0.7}\text{HPO}_4$	418	93
$\text{V}_{0.2}\text{Sn}_{0.8}\text{HPO}_4$	404	91
$\text{W}_{0.1}\text{Sn}_{0.8}\text{HPO}_4$	406	90
$\text{BaHPO}_4$	312	86
$\text{Ca}_{0.2}\text{Pb}_{0.8}\text{HPO}_4$	372	90

Table 26 (continued)

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{Sr}_{0.2}\text{Pb}_{0.8}\text{HPO}_4$	372	90
$\text{Ba}_{0.2}\text{Pb}_{0.8}\text{HPO}_4$	359	91
$\text{Zn}_{0.2}\text{Pb}_{0.8}\text{HPO}_4$	382	93
$\text{Fe}_{0.2}\text{Pb}_{0.8}\text{HPO}_4$	374	94
$\text{Ni}_{0.2}\text{Pb}_{0.8}\text{HPO}_4$	368	93
$\text{Co}_{0.2}\text{Pb}_{0.8}\text{HPO}_4$	376	92
$\text{Mn}_{0.2}\text{Pb}_{0.8}\text{HPO}_4$	374	93
$\text{Ti}_{0.2}\text{Pb}_{0.7}\text{HPO}_4$	369	94
$\text{Cu}_{0.2}\text{Pb}_{0.8}\text{HPO}_4$	371	93
$\text{Cr}_{0.2}\text{Pb}_{0.7}\text{HPO}_4$	368	95
$\text{V}_{0.2}\text{Pb}_{0.8}\text{HPO}_4$	365	93
$\text{W}_{0.1}\text{Pb}_{0.8}\text{HPO}_4$	345	93

Table 27

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{Sn}_2(\text{P}_2\text{O}_7)_{0.9}(\text{HPO}_4)_{0.2}$	495	82
$\text{Sn}_2(\text{P}_2\text{O}_7)_{0.8}(\text{HPO}_4)_{0.4}$	490	88
$\text{Pb}_2(\text{P}_2\text{O}_7)_{0.9}(\text{HPO}_4)_{0.2}$	425	80
$\text{Pb}_2(\text{P}_2\text{O}_7)_{0.8}(\text{HPO}_4)_{0.4}$	422	82

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 7.

The batteries using the metal or semi-metal hydrogenphosphate, phosphinate, or phosphonate of Example 7 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides.

#### Example 8

The electrode characteristics of various metal and semi-metal cyanides, cyanates, and thiocyanates specified in Tables 28 through 30 and used as the anode active material were evaluated in Example 8.

Tables 28 through 30 show the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 28

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{Al}(\text{CN})_3$	382	76
$\text{Al}(\text{SCN})_3$	286	82
$\text{Al}(\text{ONC})_3$	364	80

Table 28 (continued)

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
Sn(CN) <sub>4</sub>	529	85
Sn(SCN) <sub>4</sub>	326	92
Sn(ONC) <sub>4</sub>	436	90
Sn(CN) <sub>2</sub>	537	82
Sn(SCN) <sub>2</sub>	487	95
Sn(ONC) <sub>2</sub>	506	93
Si(CN) <sub>4</sub>	315	76
Si(SCN) <sub>4</sub>	292	82
Si(ONC) <sub>4</sub>	310	79
Pb(CN) <sub>2</sub>	454	82
Pb(SCN) <sub>2</sub>	346	88
Pb(ONC) <sub>2</sub>	386	87
Cd(CN) <sub>2</sub>	372	75
Cd(SCN) <sub>2</sub>	315	79
Cd(ONC) <sub>2</sub>	340	79
Bi(CN) <sub>3</sub>	324	75
Bi(SCN) <sub>3</sub>	286	86
Bi(ONC) <sub>3</sub>	316	80
In(CN) <sub>3</sub>	412	82
In(SCN) <sub>3</sub>	375	89
In(ONC) <sub>3</sub>	369	86
Zn(CN) <sub>2</sub>	315	76
Zn(SCN) <sub>2</sub>	285	83
Zn(ONC) <sub>2</sub>	310	79
Ga(CN) <sub>3</sub>	348	74
Ga(SCN) <sub>3</sub>	302	79
Ga(ONC) <sub>3</sub>	326	76
Ge(CN) <sub>4</sub>	390	78
Ge(SCN) <sub>4</sub>	352	86
Ge(ONC) <sub>4</sub>	389	82
Mg(CN) <sub>2</sub>	320	79
Mg(SCN) <sub>2</sub>	289	89
Mg(ONC) <sub>2</sub>	341	85

Table 29

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
Ti(CN) <sub>3</sub>	265	75
Ti(SCN) <sub>3</sub>	251	77
Ti(ONC) <sub>3</sub>	263	75
V(CN) <sub>2</sub>	275	81
V(SCN) <sub>2</sub>	245	82
V(ONC) <sub>2</sub>	263	80
Mn(CN) <sub>2</sub>	278	82
Mn(SCN) <sub>2</sub>	261	87
Mn(ONC) <sub>2</sub>	275	85
Sb(CN) <sub>3</sub>	315	76
Sb(SCN) <sub>3</sub>	281	80
Sb(ONC) <sub>3</sub>	298	78

Table 29-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
Cr(CN) <sub>3</sub>	301	82
Cr(SCN) <sub>3</sub>	275	84
Cr(ONC) <sub>3</sub>	280	83
Fe(CN) <sub>2</sub>	269	75
Fe(SCN) <sub>2</sub>	245	79
Fe(ONC) <sub>2</sub>	257	79
W(CN) <sub>4</sub>	215	81
W(SCN) <sub>4</sub>	201	82
W(ONC) <sub>4</sub>	210	81
Co(CN) <sub>2</sub>	269	78
Co(SCN) <sub>2</sub>	245	84
Co(ONC) <sub>2</sub>	253	80
Ni(CN) <sub>2</sub>	275	82
Ni(SCN) <sub>2</sub>	257	86
Ni(ONC) <sub>2</sub>	261	81
Cu(CN) <sub>2</sub>	251	77
Cu(SCN) <sub>2</sub>	235	80
Cu(ONC) <sub>2</sub>	246	78
Mo(CN) <sub>3</sub>	235	77
Mo(SCN) <sub>3</sub>	211	79
Mo(ONC) <sub>3</sub>	225	77
Ca(CN) <sub>2</sub>	325	78
Ca(SCN) <sub>2</sub>	314	84
Ca(ONC) <sub>2</sub>	322	80
Ba(CN) <sub>2</sub>	333	79
Ba(SCN) <sub>2</sub>	301	87
Ba(ONC) <sub>2</sub>	311	81
Nb(CN) <sub>2</sub>	222	82
Nb(SCN) <sub>2</sub>	201	83
Nb(ONC) <sub>2</sub>	216	81
Sr(SCN) <sub>2</sub>	314	84
Sr(ONC) <sub>2</sub>	322	80

Table 30

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
ZnSn(CN) <sub>4</sub>	402	87

Table 30 (continued)

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
MgSn(SCN) <sub>4</sub>	382	92
CaSn(SCN) <sub>4</sub>	382	92
Sr(SCN) <sub>4</sub>	382	92
FeSn(ONC) <sub>4</sub>	376	91
NiSn(CN) <sub>4</sub>	398	88
CoSn(SCN) <sub>4</sub>	375	93
MnSn(ONC) <sub>4</sub>	390	92
TiSn(CN) <sub>5</sub>	385	87
CuSn(SCN) <sub>4</sub>	360	93
NiPb(CN) <sub>4</sub>	382	83
CoPb(SCN) <sub>4</sub>	362	85
MnPb(ONC) <sub>4</sub>	375	84
ZnPb(CN) <sub>4</sub>	395	84
MgPb(SCN) <sub>4</sub>	376	89
CaPb(SCN) <sub>4</sub>	376	89
SrPb(SCN) <sub>4</sub>	376	89
FePb(ONC) <sub>4</sub>	375	89
TiPb(CN) <sub>5</sub>	376	84
CuPb(SCN) <sub>4</sub>	326	89
CuIn(CN) <sub>5</sub>	355	84
FeIn(SCN) <sub>5</sub>	335	91
CoIn(ONC) <sub>5</sub>	345	88
MgIn(CN) <sub>5</sub>	365	85
CuBi(CN) <sub>5</sub>	324	78
FeBi(SCN) <sub>5</sub>	315	87
BaBi(ONC) <sub>5</sub>	320	83
CaBi(CN) <sub>3</sub>	321	77
MgBi(CN) <sub>3</sub>	315	78

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 8.

The batteries using the metal or semi-metal cyanide, cyanate, or thiocyanate of Example 8 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides.

#### Example 9

The electrode characteristics of various metal and semi-metal tungstates specified in Table 31 and used as the anode active material were evaluated in Example 9.

Table 31 shows the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.



Table 31

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{Al}_3(\text{WO}_4)_3$	292	86
$\text{AlWO}_4$	301	83
$\text{SnWO}_4$	477	94
$\text{Sn}_2\text{W}_3\text{O}_8$	436	95
$\text{Sn}(\text{WO}_4)_2$	402	96
$\text{Si}(\text{WO}_4)_2$	282	95
$\text{PbWO}_4$	405	95
$\text{PbWO}_3$	419	94
$\text{CdWO}_4$	326	91
$\text{CdWO}_3$	345	90
$\text{Bi}_2\text{WO}_6$	382	90
$\text{Bi}_2(\text{WO}_4)_3$	368	92
$\text{In}_2(\text{WO}_4)_3$	426	90
$\text{In}(\text{WO}_3)_3$	398	94
$\text{Sb}_2(\text{WO}_4)_3$	350	90
$\text{ZnWO}_4$	208	86
$\text{ZnWO}_3$	226	89
$\text{Ga}_2(\text{WO}_4)_3$	321	89
$\text{Ga}_2(\text{WO}_3)_3$	333	88
$\text{Ge}(\text{WO}_4)_2$	341	89
$\text{Ge}(\text{WO}_3)_2$	353	86
$\text{MgWO}_4$	301	87
$\text{MgWO}_3$	313	86
$\text{CaWO}_4$	301	87
$\text{CaWO}_3$	313	86
$\text{SrWO}_4$	301	87
$\text{SrWO}_3$	313	86

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 9.

The batteries using the metal or semi-metal tungstate of Example 9 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides.

#### Example 10

The electrode characteristics of various metal and semi-metal molybdates specified in Table 32 and used as the anode active material were evaluated in Example 10.

Table 32 shows the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 32

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{Al}_2(\text{MoO}_4)_3$	302	87
$\text{SnMo}_2\text{O}_8$	426	94
$\text{SnMoO}_4$	472	92
$\text{SiMo}_2\text{O}_8$	340	90
$\text{PbMoO}_4$	456	94
$\text{CdMoO}_4$	346	91
$\text{Bi}_2(\text{MoO}_4)_3$	402	93
$\text{In}_2(\text{MoO}_4)_3$	436	94
$\text{InMo}_4\text{O}_6$	398	96
$\text{Sb}_2(\text{MoO}_4)_3$	348	90
$\text{ZnMoO}_4$	268	87
$\text{Ga}_2(\text{MoO}_4)_3$	359	89
$\text{GeMoO}_4$	371	90
$\text{MgMoO}_4$	324	88
$\text{CaMoO}_4$	324	88
$\text{SrMoO}_4$	324	88

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 10.

The batteries using the metal or semi-metal molybdate of Example 10 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides.

#### Example 11

The electrode characteristics of various metal and semi-metal titanates specified in Table 33 and used as the anode active material were evaluated in Example 11.

Table 33 shows the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 33

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{AlTiO}_5$	326	73
$\text{SnTiO}_4$	443	82
$\text{SiTiO}_8$	321	75
$\text{PbTiO}_3$	476	80
$\text{PbTi}_3\text{O}_7$	402	81
$\text{CdTiO}_3$	354	76
$\text{Bi}_2\text{TiO}_5$	498	81
$\text{Bi}_2\text{Ti}_2\text{O}_7$	424	82

Table 33 (continued)

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{In}_2\text{TiO}_5$	478	83
$\text{Sb}_3\text{Ti}_2\text{O}_{10}$	369	80
$\text{ZnTiO}_3$	324	76
$\text{GaTiO}_5$	371	75
$\text{GeTiO}_3$	380	74
$\text{MgTiO}_4$	334	71
$\text{CaTiO}_4$	334	71
$\text{SrTiO}_4$	334	71

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 11.

The batteries using the metal or semi-metal titanate of Example 11 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides.

#### Example 12

The electrode characteristics of various metal and semi-metal zirconates specified in Table 34 and used as the anode active material were evaluated in Example 12.

Table 34 shows the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 34

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{Al}_2(\text{ZrO}_3)_3$	304	71
$\text{SnZrO}_3$	484	78
$\text{SiZrO}_4$	342	76
$\text{PbZrO}_3$	466	77
$\text{CdZrO}_3$	357	71
$\text{Bi}_2(\text{ZrO}_3)_3$	419	77
$\text{In}_2(\text{ZrO}_3)_3$	443	78
$\text{Sb}_2(\text{ZrO}_3)_3$	354	75
$\text{ZnZrO}_3$	294	73
$\text{Ga}_2(\text{ZrO}_3)_3$	372	74
$\text{GeZrO}_3$	379	72
$\text{MgZrO}_3$	339	73
$\text{CaZrO}_3$	339	73
$\text{SrZrO}_3$	339	73

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 12.

The batteries using the metal or semi-metal zirconate of Example 12 as the anode active material have the

improved cycle characteristics, compared with the prior art metal oxides.

#### Example 13

5 The electrode characteristics of various metal and semi-metal vanadates specified in Table 35 and used as the anode active material were evaluated in Example 13.

Table 35 shows the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 35

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{AlVO}_4$	319	82
$\text{SnV}_2\text{O}_6$	452	89
$\text{Sn}_2\text{V}_2\text{O}_6$	489	87
$\text{SiV}_2\text{O}_7$	324	84
$\text{Pb}_2\text{V}_2\text{O}_6$	477	86
$\text{PbV}_2\text{O}_6$	427	88
$\text{CdV}_2\text{O}_6$	326	83
$\text{BiVO}_4$	436	86
$\text{Bi}_2\text{VO}_5$	496	85
$\text{InVO}_4$	498	85
$\text{In}_2\text{VO}_5$	504	83
$\text{SbVO}_4$	354	83
$\text{ZnV}_2\text{O}_6$	311	81
$\text{GaVO}_4$	368	83
$\text{GeV}_2\text{O}_6$	341	84
$\text{MgV}_2\text{O}_6$	312	79
$\text{CaV}_2\text{O}_6$	312	79
$\text{SrV}_2\text{O}_6$	312	79

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 13.

The batteries using the metal or semi-metal vanadate of Example 13 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides.

#### Example 14

50 The electrode characteristics of various metal and semi-metal chromates specified in Table 36 and used as the anode active material were evaluated in Example 14.

Table 36 shows the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 36

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
AlCrO <sub>3</sub>	342	87
SnCrO <sub>4</sub>	463	94
Sn <sub>2</sub> CrO <sub>6</sub>	504	92
Si(CrO <sub>4</sub> ) <sub>2</sub>	341	89
Pb <sub>3</sub> CrO <sub>6</sub>	511	91
PbCrO <sub>4</sub>	484	93
CdCr <sub>2</sub> O <sub>4</sub>	324	87
BiCrO <sub>3</sub>	432	91
Bi <sub>2</sub> CrO <sub>6</sub>	426	93
InCrO <sub>3</sub>	445	92
In <sub>2</sub> CrO <sub>6</sub>	486	90
Sb <sub>2</sub> (CrO <sub>4</sub> ) <sub>3</sub>	352	88
ZnCrO <sub>4</sub>	336	87
Ga <sub>3</sub> (CrO <sub>4</sub> ) <sub>2</sub>	381	86
GeCrO <sub>4</sub>	382	85
MgCr <sub>2</sub> O <sub>7</sub>	304	87
CaCr <sub>2</sub> O <sub>7</sub>	304	87
SrCr <sub>2</sub> O <sub>7</sub>	304	87

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 14.

The batteries using the metal or semi-metal chromate of Example 14 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides.

#### Example 15

The electrode characteristics of various metal and semi-metal niobates specified in Table 37 and used as the anode active material were evaluated in Example 15.

Table 37 shows the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 37

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
AlNbO <sub>4</sub>	324	71
SnNb <sub>2</sub> O <sub>6</sub>	424	75
Sn <sub>2</sub> Nb <sub>2</sub> O <sub>7</sub>	468	74
SiNbO <sub>4</sub>	342	71
PbNb <sub>2</sub> O <sub>6</sub>	403	74
Pb <sub>2</sub> Nb <sub>2</sub> O <sub>7</sub>	426	72

Table 37 (continued)

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{Cd}_2\text{Nb}_2\text{O}_7$	314	71
$\text{BiNbO}_4$	415	73
$\text{InNbO}_4$	445	74
$\text{SbNbO}_4$	370	73
$\text{ZnNb}_2\text{O}_6$	204	71
$\text{GaNbO}_4$	364	72
$\text{GeNb}_2\text{O}_6$	368	73
$\text{MgNb}_2\text{O}_6$	301	72
$\text{CaNb}_2\text{O}_6$	301	72
$\text{SrNb}_2\text{O}_6$	301	72

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 15.

The batteries using the metal or semi-metal niobate of Example 15 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides.

#### Example 16

The electrode characteristics of various metal and semi-metal tantalates specified in Table 38 and used as the anode active material were evaluated in Example 16.

Table 38 shows the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 38

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{AlTaO}_4$	302	81
$\text{Sn}_2\text{Ta}_2\text{O}_7$	476	88
$\text{SiTa}_2\text{O}_7$	272	82
$\text{Pb}_2\text{Ta}_2\text{O}_7$	406	87
$\text{Cd}_2\text{Ta}_2\text{O}_7$	314	84
$\text{BiTaO}_4$	404	86
$\text{InTaO}_4$	446	85
$\text{SbTaO}_4$	364	85
$\text{Zn}_2\text{Ta}_2\text{O}_7$	246	83
$\text{GaTaO}_4$	356	81
$\text{Ge}_2\text{Ta}_2\text{O}_7$	346	81
$\text{Mg}_2\text{Ta}_2\text{O}_7$	304	79
$\text{Ca}_2\text{Ta}_2\text{O}_7$	304	79
$\text{Sr}_2\text{Ta}_2\text{O}_7$	304	79

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No

deposit of metallic lithium was observed in any of the test cells of Example 16.

The batteries using the metal or semi-metal tantalate of Example 16 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides.

#### 5 Example 17

The electrode characteristics of various metal and semi-metal manganates specified in Table 39 and used as the anode active material were evaluated in Example 17.

10 Table 39 shows the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 39

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$\text{Al}_2\text{MnO}_6$	326	80
$\text{SnMnO}_3$	486	89
$\text{SnMn}_2\text{O}_4$	424	90
$\text{SiMnO}_3$	314	81
$\text{PbMnO}_3$	443	87
$\text{CdMnO}_3$	369	82
$\text{Bi}_2\text{MnO}_4$	424	84
$\text{Bi}_2\text{MnO}_6$	412	86
$\text{In}_2\text{MnO}_4$	461	84
$\text{In}_2\text{MnO}_6$	452	84
$\text{Sb}_2\text{MnO}_4$	392	83
$\text{Sb}_2\text{MnO}_6$	376	84
$\text{ZnMnO}_3$	314	81
$\text{Ga}_2\text{MnO}_4$	386	81
$\text{GeMnO}_3$	349	82
$\text{MgMnO}_3$	326	78
$\text{CaMnO}_3$	326	78
$\text{SrMnO}_3$	326	78

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 17.

The batteries using the metal or semi-metal manganate of Example 17 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides.

Although all the above examples refer to the cylindrical batteries, the principle of the present invention is not restricted to this structure but may be applicable to secondary batteries of various types, such as coin-type, rectangular-type, and cylinder-type.

In the above examples,  $\text{LiMn}_{1.8}\text{Co}_{0.2}\text{O}_4$  was used as the cathode active material. The similar effects can be exerted for a variety of other cathode active materials allowing reversible charge and discharge operations, such as  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ , and the like.

As discussed above, the present invention uses an anode of high capacity and excellent cycle life and thereby provides a non-aqueous electrolyte secondary battery that is free of a short circuit due to dendrite and has a higher energy density and a high reliability.

## Claims

1. A non-aqueous electrolyte secondary battery comprising a cathode capable of being charged and discharged, a non-aqueous electrolyte, and an anode capable of being charged and discharged, said anode having an active material that comprises a salt of a metal or a semi-metal and a compound selected from the group consisting of oxo-acids, thiocyanic acid, cyanogen, and cyanic acid, wherein each said oxo-acid comprises an element selected from the group consisting of nitrogen, sulfur, carbon, boron, phosphorus, selenium, tellurium, tungsten, molybdenum, titanium, chromium, zirconium, niobium, tantalum, manganese, and vanadium, salts of said oxo-acids of phosphorus and boron being restricted to hydrogenphosphates and hydrogenborates.
2. The non-aqueous electrolyte secondary battery in accordance with claim 1, wherein said anode comprises a mixture of said active material, carbon material, and a binding agent.
3. The non-aqueous electrolyte secondary battery in accordance with claim 1, wherein said metal or semi-metal is at least one selected from the group consisting of Al, Sn, Si, Pb, Cd, Bi, In, Zn, Mg, Ge, Ga, Ca, Ba, Sr, B, Ir, Sb, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Mo, W, and Nb.
4. The non-aqueous electrolyte secondary battery in accordance with claim 1, wherein said metal salt or semi-metal salt of said oxo-acid of nitrogen is at least one selected from the group consisting of nitrates and nitrites.
5. The non-aqueous electrolyte secondary battery in accordance with claim 1, wherein said metal salt or semi-metal salt of said oxo-acid of sulfur is at least one selected from the group consisting of sulfates, sulfites, disulfates, peroxomonosulfates, peroxodisulfates, thiosulfates, dithionates, disulfites, thiosulfites, dithionites, and sulfoxylates.
6. The non-aqueous electrolyte secondary battery in accordance with claim 1, wherein said metal salt or semi-metal salt of said oxo-acid of phosphorus is at least one selected from the group consisting of monohydrogenphosphates, dihydrogenphosphates, phosphinates, and phosphonates.
7. The non-aqueous electrolyte secondary battery in accordance with claim 1, wherein said metal salt or semi-metal salt of said oxo-acid of boron is at least one selected from the group consisting of monohydrogenborates and dihydrogenborates.
8. The non-aqueous electrolyte secondary battery in accordance with claim 1, wherein said metal salt or semi-metal salt of said oxo-acid of selenium is at least one selected from the group consisting of selenates  $M_2(SeO_4)_m$ , selenites  $M_2(SeO_3)_m$ ,  $M_2(SeO_5)_m$ ,  $M(HSeO_4)_m$ , and  $M(HSeO_3)_m$ , where M denotes a metal or semi-metal having a valence m.
9. The non-aqueous electrolyte secondary battery in accordance with claim 1, wherein said metal salt or semi-metal salt of said oxo-acid of tellurium is at least one selected from the group consisting of  $M_6(TeO_6)_m$ ,  $M_2(TeO_4)_m$ ,  $M_5(H_5TeO_6)_m$ ,  $M_4(H_2TeO_6)_m$ ,  $M_2(H_3TeO_6)_m$ , and  $M_2(H_4TeO_6)_m$ , where M denotes a metal or semi-metal having a valence m.



FIG. 1

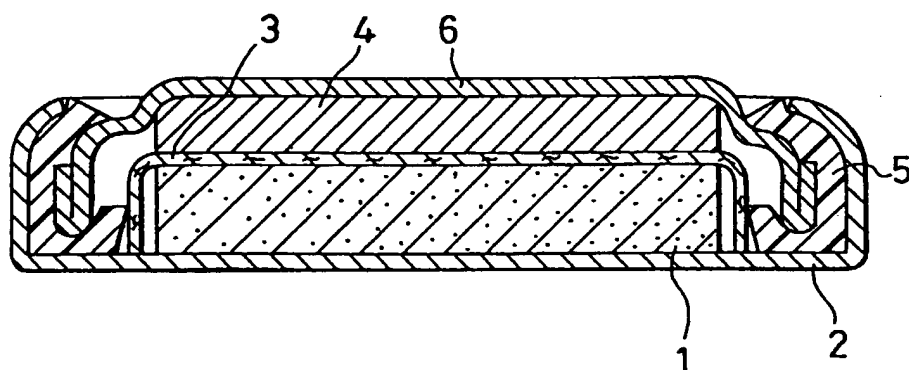
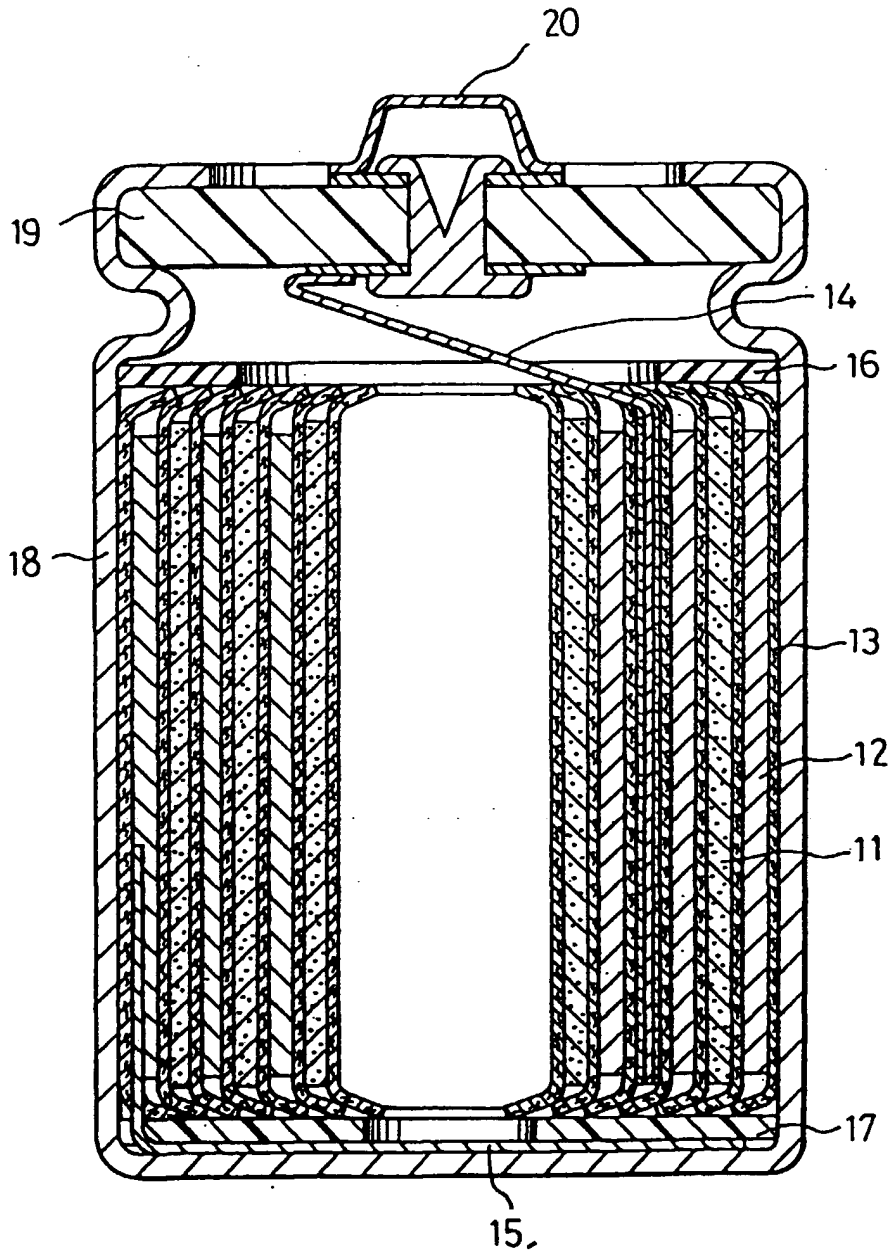


FIG. 2





European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 97 12 2297

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 626 (E-1636), 29 November 1994 & JP 06 243870 A (SANYO ELECTRIC CO LTD), 2 September 1994, * abstract *	1,4,5	H01M4/62 H01M4/48 H01M4/58
X	US 5 474 861 A (BITO YASUHIKO ET AL) * claims 1-17 *	1,2	
A	EP 0 413 331 A (RAY O VAC CORP) * claims 1-20 *	1-9	
A	EP 0 582 410 A (SANYO ELECTRIC CO) * claims 1-14 *	1-9	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			H01M
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>6 April 1998</b>	Examiner <b>Battistig, M</b>
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document</p> <p>T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons</p> <p>&amp;: member of the same patent family, corresponding document</p>			

EPO FORM 1503 03/92 (P04C01)